AN ASSESSMENT OF THE EFFECTS OF HYDROFLUORIC ACID BASED CLEANER ON UNGLAZED ARCHITECTURAL TERRACOTTA

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CHAPTER ONE: INTRODUCTION

Unglazed architectural terra cotta accounts for a significant portion of the built heritage of Britain and North America, and the need for research into suitable cleaning techniques for unglazed architectural terra cotta has been cited:

> Unglazed architectural terra cotta buildings account for a large percentage of the industrial world's nineteenth-century architectural heritage and as such represent a unique and difficult cleaning problem that demands considerably more study than has previously occurred. A complex issue, their neglect and mishandling can in part be attributed to both past and current attitudes regarding the perceived durability of ceramic materials and a long standing professional preoccupation with natural building stone and its specific decay mechanisms. This has resulted in both an ignorance of terra cotta's unique problems of variability...and the misapplication of cleaning approaches designed for natural building stone.[1]

Its popularity as a building material in these regions coincided with the rise of industrialized society, resulting in a degree of soiling commensurate with the heavily polluted atmosphere of urban centers in the late nineteenth century.

In an attempt to combat this severe soiling, a number of cleaning techniques for unglazed architectural terra cotta were developed at the turn of the century, including sandblasting and the use of hydrofluoric acid. Hydrofluoric acid has been considered a primary cleaning agent for unglazed architectural terra cotta since the 1920s.[2] Although condemned in 1928 for its tendency to etch the surface of glazed and unglazed terra cottas,[3] this method of removing soiling has enjoyed renewed

[1] Frank G. Matero, ElizaBeth A. Bede, and Alberto Tagle, "An Approach to the Evaluation of Cleaning Methods for Unglazed Architectural Terracotta in the USA," in *Architectural Ceramics*, ed. Jeanne Marie Teutonico (London: English Heritage 1996), 57.
[2] "Cleaners for Terra Cotta," *National Bureau of Standards Technical News Bulletin* (1928), 131-33.
[3] Ibid.

popularity over the past few decades. Despite this recent gain in popularity, however, surprisingly little research has been undertaken to assess the long term effects of the cleaning process on the building as a whole, or the effects of the cleaning agent on the terracotta itself. Generally, the success of cleaning programs has been judged by efficacy alone, and the primary evaluative technique has been visual examination. Even recent efforts to quantify color change using techniques such as chromometry have focused on soiling removal alone. In order to ascertain what if any deterioration occurs to the substrate during cleaning, the physical effects of chemical based cleaners on masonry must be assessed. This thesis is intended to be one in a much needed series of studies regarding the effects of hydrofluoric acid based cleaners on architectural terra cotta.

The first significant study to assess the potential effects of hydrofluoric acid based cleaning on unglazed terra cotta was performed by John Ashurst in 1985.[4] This study visually inspected several sites in heavily trafficked urban areas that had been cleaned ten to fifteen years earlier. The sample buildings covered a wide range of building materials and cleaning techniques. On terra cotta structures, sandblasting had resulted in unacceptable damage; both appearance and condition related to cleaning were rated poor by the author.[5] The results of acid based cleaning were equally dire: streaks of silica and slow re-soiling on "generally all" surfaces resulted in an

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[4] John Ashurst, "Cleaning and Surface Repair—Past Mistakes and Future Prospects," *APT Bulletin* 17:2, 39-41.
[5] Ibid, 40.

evaluation of fair appearance, and fair to poor condition.[6]

A study of the exterior terracotta of the Brooklyn Historical Society represented the next phase of research into the effects of cleaning techniques on unglazed architectural terra cotta.[7] The research undertook to "ascertain which cleaning techniques effectively removed atmospheric soiling without negatively altering the physical properties of the terra cotta, especially the fireskin."[8] Several techniques were evaluated based on a user survey, including commercial acidic cleaners, commercial alkaline cleaners with an acidic after wash, steam cleaning, abrasive cleaning, and detergent emulsions. It was in this study that physical changes to the fireskin were first noted. Using scanning electron microscopy, it was apparent that the hydrofluoric acid based cleaner was increasing the size of and connection between surface pores.[9] This study called for future research to quantify the observed physical and mechanical alterations to the microstructure of unglazed terra cotta, and recommended that weathering tests be performed to evaluate the performance of altered materials.[10]

A third study undertaken by C.R. Moynehan at the University of Bristol used a variety of surface analytical and conventional chemical techniques to evaluate the effects of hydrofluoric acid based cleaners on unglazed terra cotta.[11] Moynehan's research concluded that these cleaners are effective through dissolution of the siliceous

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[6] Ibid,40.
[7] Matero, Bede, and Tagle, 1996.
[8] Ibid, 57.
[9] Ibid, 82.
[10] Ibid, 83.

terracotta surface, resulting in increased pore size and in some cases virtual annihilation of the fireskin.[12] The study also found that fluoride, sulfate, phosphate and chloride salts are re-precipitated and deposited both in and on the surface of the terra cotta, causing irreversible and damaging changes to the terra cotta as a whole.[13]

The most recent study in this series was undertaken in 1995 as a joint venture between Historic Building and Site Services at Bournemouth University and the Architectural Conservation Team of English Heritage.[14] This study evaluated the effects of several different cleaning systems on the porosity of unglazed architectural terra cotta. Both historic and modern terra cottas were obtained and subjected to several cleaning systems, including a commercial hydrofluoric acid based cleaner. Porosity was evaluated using a mercury intrusion porosimeter. For all terra cottas, pore size increased after exposure to a hydrofluoric acid based cleaner.[15] However, the study did not draw conclusions regarding the long-term effect of the cleaning techniques:

> It is difficult...to make predictions about ongoing loss of fireskin after it has been damaged by HF or abrasive cleaning, although it seems most likely that partial loss of fireskin will result in accelerated weathering by allowing water penetration and all the various processes associated with moisture ingress.[16]

Instead, the study called for research into the comparative behavior of cleaned and un-

[11] C.R. Moynehan, G.C. Allen, I.T. Brown, S. R. Church, J. Beavis, and J. Ashurst, "Surface Analysis of Architectural Terracotta," *Journal of Architectural Conservation* (1995)1:1, 56-69.
[12] Ibid, 68.
[13] Ibid, 67.
[14] John Ashurst, Catherine Woolfit, and Philip Forshaw, "Unglazed Architectural Terracotta: An Investigation into the Effects of Cleaning," (Unpublished report for the Architectural Conservation Team, English Heritage, March 1995).
[15] Ibid, 20.

cleaned samples in a weathering chamber.[17]

This thesis is intended to be the next step in this broader body of research. The study focused on hydrofluoric acid based cleaners, as they are the most commonly used method of removing stubborn, chemically-affixed soiling from the surface of unglazed architectural terra cotta. The scope of the research was two-fold: the author sought to quantify the changes to the surface of the terra cotta, and to compare the performance of terra cotta in various states of cleanliness when exposed to accelerated weathering agents.

Previous research has confirmed through scanning electron microscopy that the use of hydrofluoric acid based cleaners on unglazed architectural terra cotta results in changes to the physical properties of the fireskin, most notably by increasing the size, shape, and number of surface pores. The first phase of this research attempted to *describe and quantify the changes caused by HF based cleaners.* Quantification provides for a rectified characterization of the material, which will improve professionals' ability to predict the behavior of the altered material. Having established that these changes are both noticeable and quantifiable, the second phase of this research asked the question: *what impact do the physical changes to the material have on long term performance of the material?* Through a limited testing program, the performance of two American commercial unglazed terra cottas that have been washed once. twice, and three times with a commercial hydrofluoric acid based cleaner was compared to the performance of untreated terra cotta.

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[16] Ibid, 33.

In order to answer these questions, a scope of work was developed. This study included the following:

1. An extensive survey of relevant literature. Sources regarding history, manufacture and characterization of unglazed terra cotta were consulted, as were all sources that dealt with the cleaning and conservation of the material.
2. A visual and mineralogical characterization of the terra cotta samples used for testing.
3. The investigation, design, and determination of an assessment system to quantify the changes to the physical properties of the terra cotta.
4. The design and execution of a testing program to determine the weathering potential of the treated samples, based on the relevant literature and in cooperation with the thesis advisors.
5. Analysis of the results of all of the above tests.
6. Recommendations for further testing.

Through this methodology, effects of hydrofluoric acid based cleaners on unglazed architectural terra cotta were assessed.

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[17] Ibid, 34.

Chapter Two: What Is Terra Cotta?

Unglazed architectural terra cotta is classified as an architectural ceramic, a class of building materials with unique properties. Ceramics are defined as solids composed of a mixture of metallic, semi-metallic, and non-metallic elements in such proportions as to give them properties of chemical and physical hardness, durability, and resistance.[18] The distinction of "architectural" is given to distinguish terracotta and other forms of terra cotta used in pottery and domestic ceramics.[19]

Components of Terra Cotta

Unglazed architectural terra cotta is a ceramic material composed of clays and additives. Clay is the principal ingredient, forming the base of the material and giving it its plasticity and moldability. Due to the highly plastic nature of clays, additives are required to prevent shrinkage and counteract the effects of impurities.

Clay minerals are the most abundant minerals at the surface of the earth.[20] Clay minerals are defined by geologists as materials less than 2 microns in diameter, the vast majority of which are hydrated aluminous silicates.[21] This composition gives clays their characteristic plasticity, differentiating them from other mineral

[18] Rodney Cotterill, *Cambridge Guide to the Material World* (Cambridge: Cambridge University Press).
[19] Martin Weaver with Frank G. Matero. *Conserving Buildings: A Guide to Techniques and Materials* (New York: John Wiley and Sons, 1993), 109.
[20] Duane M. Moore, and Robert C. Reynolds. Jr., *X-ray Diffraction and the Identification and Analysis of Clay Minerals* (New York: Oxford University Press, 1989), 3.
[21] Ibid, 3.

substances.[22] The crystalline structure of clays, in which crystals are formed from alternating sheets of silica and alumina, allows penetration of water molecules between the sheets. Clays therefore absorb water readily, giving them their moldability. In addition to hydrous alumina silicate, other chemical compounds are found in clays. These components affect the behavior of the terracotta body and determine its natural color. The type of clay that has historically been considered the best clay for the manufacture of terra cotta has combined alumina and silica in a relationship of roughly two parts silica for each part alumina.[23] This relationship is most commonly achieved by mixing clays, with fireclays serving as a primary component. [24] Fireclays differ from other clays in their resistance to high temperatures, a function of the ratio of free silica and alumina.[25]

Traditionally, chemical additives have included barium carbonates and manganese compounds. Barium carbonates were used to mitigate the effects of soluble salts found in the clays; barium carbonate reacts chemically with the soluble salts to form insoluble compounds, thereby protecting the terra cotta units from potentially damaging crystallization cycles caused by soluble salts. Manganese compounds react with the metal oxides present in clays and are used to control the color of the body. Additionally, mineral additives such as feldspars were used to lower the necessary firing temperature of the blocks.

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[22] Charles Davis, *A Practical Treatise on the Manufacture of Brick, Tiles, and Terra Cotta,* third edition (Philadelphia: Henry Carey Baird, 1895), 26.
[23] Ibid, 80.
[24] Ibid, 80.
[25] Ibid, 57-8.

Among the most significant additives to the mix is grog, which is defined as ground, previously-fired and semi-vitrified terra cotta.[26] According to MacIntyre:

> The general function of the non-plastic content of a batch is to lend rigidity to the body during the stages of manufacturing and to enable some control to be exercised over the properties of finished ware. By varying the grading of the grog and its proportion to raw clay, it is possible to exercise very considerable control over porosity, permeability, elasticity, etc.[27]

The highly plastic nature of clays initiates shrinkage during the firing process. As grog is a previously fired material, it is not susceptible to shrinkage and controls the shrinkage and warping of the body as a whole as it loses moisture during air and kiln drying.

The Manufacture of Architectural Terra Cotta

The manufacturing process of architectural terra cotta has been well described in several sources,[28] and will therefore be described only briefly. The manufacturing process begins with the extraction and weathering of the clays. Once removed from the ground, the clays are "blunged," or left exposed to natural weathering cycles. This process allows frost and rain to break down the massive lumps of clay and promotes reactions between the elements of the clay. These reactions allow for the easy removal of staining metallic components and reduces in the alkaline content of the

[26] Weaver with Matero, p. 112.
[27] William MacIntyre, *Investigations Into the Durability of Architectural Terra Cotta and Faience.* (London: Her Majesty's Stationary Office, 1929), 6.
[28] Weaver with Matero give an excellent explanation of the manufacture process, as does Robert Mack in "The Manufacture and Use of Architectural Terra Cotta in the United States," in *The Technology of American Buildings: Studies of the Materials, Processes, and the Mechanization of Building*

clays.

After the clays have been adequately weathered, they are sieved and ground into a powder. At this stage, the grog and chemical additives are added to the mix. The mix is tempered with water, giving it the plasticity necessary for manipulation. The mixture is then packed into plaster molds that are manufactured according to the architect's specifications. These molds are made 1/12 to 1/13 larger than the desired size of the piece to account for the inevitable shrinkage during firing.

Once fully packed into the molds, the pieces are left to dry for approximately three days. As the unit dries, it shrinks, pulling away from the plaster mold. When the unit is sufficiently dry and stiff to support its own weight, it is turned from its mold and finished, or "tooled." Tooling is the process of smoothing down what will be the external surface of the piece, using flat wooden and metal spatulas, and scraps of leather.

After tooling, the units are taken to a drying room and left to dry for a period that can extend from a week to several months. Care is taken to ensure that the temperature of the drying room does not exceed 30°C, since higher temperatures may result in excessively rapid drying, which can cause warping and cracking.

The final step in the manufacturing process is firing. The units are moved to the kiln, where they are fired at temperatures ranging from 850° to 1200°C. Several chemical reactions take place during the firing process:

Construction, ed. H. Ward Jandl. Washington, D.C.: Foundation for Preservation Technology, 1983. For a historic description of the process, see either MacIntyre or Davis.

> Excess water, carbon dioxide and other gases were initially driven off, to be followed by the oxidation of carbonaceous matter and the burning out of the sulfur of pyrites and other impurities. Ferrous compounds also oxidized to ferric, the carbonates decomposed, and the chemically combined waters of hydrated minerals were driven off. This process causes shrinkage, gradual re-crystallization and, if the temperature is high enough, vitrification (the fusion of bonding clay by the sintering of its constituents).[29]

After the firing process, the terra cotta units are ready for installation.

The Formation and Importance of the Fireskin

Of particular relevance to this thesis is the formation of the fireskin. The fireskin is a thin layer of fine grained clay particles that vitrifies during the firing process, forming a tough skin resistant to mechanical and chemical abrasion. Formation of the fireskin begins during the three day drying period of the unit in the mold. As water is drawn from the moist mix into the dry plaster, the finest particles of clay are transported in the water and are deposited at the interface between the unit and the mold. This results in a thin layer of colloidal particles that remains on the surface of the unit and is further developed during the tooling process. Upon firing, this layer of fine surface particles actually vitrifies, forming a virtually non-porous, glassy layer known as the fireskin.[30]

The importance of the fireskin has been the subject of much discussion. MacIntyre questions its validity:

> The actual value of this skin is open to question. In some cases it can

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[29] John Fidler, "The Conservation of Architectural Terra Cotta and Faience." *Transactions of the Association for Studies in the Conservation of Historic Buildings* 1981 (6:3-16), 6.
[30] MacIntyre, Weaver, and Fidler.

> be very impervious to atmospheric moisture, and prevent the penetration into the block of moisture from the face. On the other hand, it prevents the removal by evaporation, from the face, of moisture reaching the block through the joints; this water, in time, might accumulate and lead to the block becoming saturated and so more susceptible to the actions of frost or other disruptive agencies.[31]

Today, however, the value of the fireskin is widely accepted by professionals. Damage to the fireskin is disastrous for the unit as a whole:

> Maintenance of the fireskin...is critical to the well being of terracotta and faience as the clay bodies they protect are far less durable. Their degradation can lead to one of the most complicated failure systems of all materials.[32]

Although widely believed, this assertion has not yet been confirmed in practice, but will be tested in years to come. As the terracotta buildings sandblasted and overcleaned in the early 1970s continue to weather, the inherent durability of the clay body will be assessed, and the ultimate protective worth of the fireskin will be determined.

The Soiling of Terra Cotta

There are several levels of soiling, dependent on the type of chemical bond adhering the dirt to the surface of the masonry. Covalent and ionic bonds are of sufficient strength to hold atoms together, whereas hydrogen bonds, van der Waals forces, and polar attractions form weaker bonds between molecules that result in the adhesion of soiling to a masonry surface.

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[31] MacIntyre, p.9.
[32] John Ashurst and Nicola Ashurst, *Practical Building Conservation, vol. 2.* (New York: Halsted Press, 1988), 70.

Polar attraction is caused by the arrangement of electrons within a given molecule. In some molecules, the electrons are distributed in such a way that one end of the molecule has a slightly positive charge, while the other end has a corresponding slightly negative charge. The positive and negatively charged ends are accordingly attracted to the opposite charges. For example, a slight negative charge on the surface of a material will attract the slight positive charge of dirt molecules, or vice versa. This is one way that dirt bonds to the surface of a building. Hydrogen bonds form very strong polar attractions, typically five times stronger than other polar attractions.[33]

Van der Waals forces are the weakest type of bond in chemistry. These forces are the result of a generalized attraction between the positive and negative elements of molecules. The positive charges of the nucleus is attracted to the negative charge of the electron clouds of another atom, thereby weakly bonding the two atoms (and the molecules of which they are a part) together. These forces are another means by which soling bonds to the surface of the masonry.

This chemical bonding as it applies to terracotta soiling is noted by John Fidler:

> An additional factor is the reactivity of the clay after firing. It appears that airborne dust particles are attracted to the surface and chemically bond there from an early date.[34]

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[33] James E. Brady, and John R. Holum, *Chemistry: the Study of Matter and its Changes*, second edition. (New York: John Wiley and Sons), 444.

[34] John Fidler, "Fragile Remains: An International Review of Conservation Problems in the Decay and Treatment of Architectural Terracotta and Faience." *Architectural Ceramics*, ed. Jeanne Marie Teutonico (London: English Heritage 1996), 16.

It is likely that the surface molecules are polar, attracting dirt that forms a bond with the surface molecules. The tenacity of this bond is problematic in the process of cleaning terra cotta. The strength of the adhesion of the dirt particles to the surface is greater than the cohesion of the dirt molecules to itself.[35] Therefore, gentler cleaning methods such as water washing and the use of detergents will only be effective in removing the outer layers of soiling, and harsher techniques such as abrasive and chemical methods will be required to break the chemical bond between the substrate and the soiling.

Professionals agree that terra cotta soils unevenly, although there are contradictory theories as to the nature and causes of the soiling. Nicola Ashurst claims that degree of soiling is related to water saturation:

> Both glazed and unglazed soil most heavily in areas of heaviest water saturation. Soiling is commonly located at the edges of blocks in the vicinity of mortar joints....
>
> The upward facing or water saturated surfaces of terracotta facades are usually heavily soiled and frequently require a second application of the determined general cleaning method.[36]

John Fidler has an alternative theory for the uneven soiling of terra cotta:

> It is often the case that unglazed terracotta blocks stain unevenly. The center of a hollow piece will invariably discolor or attract grime and dirt more quickly than the borders of its finished face, though the edges always appear darker than the rest. In my opinion, this phenomenon has its origins in kiln firing whereby the more solid areas of the block's face, adjacent to the side walls or the internal straps, become relatively less vitrified than the more exposed areas in the center. Consequently,

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[35] *Science for Conservators, Book 2: Cleaning.* Crafts Council Science Teaching Series.(London: Crafts Council, 1983), 21.

[36] Nicola Ashurst. *Cleaning Historic Buildings, vol. 1.* (London: Donhead Publishing, 1994), 110, 113.

> the former areas are usually slightly lighter in tone than the center of the block. On site, with exposure to sunshine, the darker areas may well warm up more than the surrounding face, causing electrostatic charges to attract dust and grease there. Algae, lichens, and mosses may also lodge there albeit in more secluded positions.[37]

In either case, it is clear that the soiling of terracotta is uneven. In combination with the severity of soiling common on unglazed architectural terracotta, the need for an effective, even cleaning technique is apparent.

The Mechanism of Hydrofluoric Acid

Hydrofluoric acid based cleaners are one of few methods that are effective in removing chemically bound soiling on terra cotta. Unlike other commercial cleaning methods, hydrofluoric acid based cleaners react chemically so as not to break the bond between the soiling and the substrate, but rather the bonds between the silicate crystals of the surface. The cleaner effectively attacks the outermost layers of the silicates of the fireskin itself, not the bond between the dirt and the fireskin. Therefore, the chemically bound soiling is never truly released from the fireskin; instead, the outermost surface of the fireskin is released, carrying the still-bonded dirt particles with it. This is an inherently destructive process:

> It must always be remembered that hydrofluoric acid works because it dissolves the silicates of the surface of the ceramic unit at the interface between the soiling and the terracotta. The amount of material dissolved may only be a few micrometers thick, but it is a destructive method.[38]

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[37] John Fidler, "The Conservation of Architectural Terra Cotta and Faience." *Transactions of the Association for Studies in the Conservation of Historic Buildings* (1981), 9.
[38] Weaver with Matero, 124.

Additionally, white blooms of insoluble salts may be deposited on the surface depending on operator technique, leaving an permanent stain.

ESSENTIAL PROPERTIES

Certain physical properties of terra cotta determine and affect its long term durability and weatherability. These include water absorption, coefficient of thermal expansion, compressive, tensile, and shear strengths. These physical properties are determined not only by the chemical composition of the terra cotta body, but by other factors generally resulting from the manufacturing process. Proper sorting and mixing of grog into the clay, proper packing of the mix into the mold, and the duration and temperature of firing will all have an effect on the essential properties of the material.

Typical values for terra cotta are as follows:

Water absorption:	5-9% [39]
Coefficient of Thermal Expansion at -50°:	2.0×10^{-6} [40]
Compressive Strength:	3,000-12,000 psi[41]
Tensile Strength:	5970 psi[42]
Shear Strength:	2650 psi[43]

These values are averages. Exact values for an individual terra cotta must be determined through laboratory testing. For this thesis, the most important property to

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[39] Susan Berryman and Susan Tindall, *Terracotta.* (Chicago: Landmarks Council of Illinois, 1984.) This was supplemented by a conversation with a Gladding McBean representative.
[40] Weaver, 116
[41] MacIntyre, 38-9.
[42] MacIntyre, 35-7.
[43] MacIntyre, 39.

be evaluated is porosity; exact values for the porosity of each type of terra cotta are reported in Chapter Five.

As an architectural ceramic, terra cotta is a highly durable building material that is resistant to chemical and physical deterioration. This is largely due to the chemical and physical stability of the clays achieved through proper firing.[44] This durability is augmented by the protection of the vitreous fireskin surface. However, the silicates that compose the fireskin surface are chemically reactive and tend to attract airborne dirt particles. The attraction between these particles and the fireskin surface creates a layer of surface soiling that is insoluble in water. The desire to remove this layer of soiling has led to the use of hydrofluoric acid based cleaners, as they have traditionally achieved high levels of cleanliness with minimal apparent damage.[45] However, the physical changes to the porosimetry of the fireskin surface that have been observed as a result of hydrofluoric acid cleaning may have an impact on the physical properties of the material, therefore altering the long term durability and weathering properties of the material.

[44] R. Casadio, B. Fabbri, G. Guarini, R. Maldera, and P. Manara, "The Deterioration of Terracotta: the case of Casa Valenti in Faenza." *Science, Technology, and European Cultural Heritage. proceedings of the European Symposium* (Bologna, 13-16 June 1989), 895.
[45] The history of cleaning technology and alternative cleaning methods will be discussed in Chapter Three.

Chapter Three: History of Terra Cotta Cleaning Techniques

Architectural terra cotta dates to ancient times, having been used in the Ancient Near East, Egypt, and Greece. The Etruscans and Romans used the material extensively, but in the Middle Ages, the use of architectural terra cotta declined in Europe. It enjoyed a revival in fifteenth century Italy, and the craft was subsequently re-introduced throughout Europe. In England, terra cotta was employed to produce sculptural details and ornament, but did not become a building material of note until the late eighteenth century with the advent of patented processes such as Coade Stone. The nineteenth century witnessed an explosion in the use of architectural terra cotta in both England and North America. Architectural terra cotta was praised for its cheapness, ease of molding to produce sculptural details, and "above all its resilience and durability in the increasingly soot-ridden and seriously polluted air of Victorian cities."[46] Unglazed architectural terra cotta was first manufactured in the United States in the 1860s and boomed in popularity in the late nineteenth century with the advent of the modern skyscraper. The lightweight tiles and panels were carried easily by the steel frame of the building, and were easier to manipulate and transport to the necessary heights than masonry blocks. It remained in common use through the first decade of the twentieth century. Architectural terra cotta achieved the height of its popularity in England and North America during an industrial era with a polluted environment. As a result, it faced tremendous cleaning challenges.

From its earliest days, terra cotta enjoyed a reputation as easy to clean. Glazed

terra cotta was highly respected in this regard; many historic sources mention the ease with which the pollution of the smoky cities of the west could be removed.[47] Even unglazed terra cotta, provided it was properly fired, was considered comparatively superior to natural building stone due to escalating use of inferior building stone and the resultant premature decay.

> In the first place, terra-cotta being impervious to wet, or nearly so, it will not vegetate as stone is liable to do; and the small particles of dust, soot, etc., which settle down upon it, and which in the case of stone so soon disfigure it, changing it from white to black, are, upon every shower of rain that falls, washed away, leaving the color just as at first.[48]

Thirty years later, the myth of self-cleaning unglazed architectural terra cotta had been shattered. However, the ease and efficacy of cleaning was still considered superior to that of brick and stone:

> From the standpoint of cleanliness, too, terra-cotta has outstanding advantages over other materials, a consideration of great importance in modern industrial centres. The difficulty and expense of satisfactorily cleaning brick and stone are well known and very often the process can be carried out only by wearing down an appreciable volume of the materials.[49]

The need for a cleaning system for architectural terra cotta was also documented by the National Bureau of Standards. In 1928, six different chemical cleaners were tested on both glazed and "standard finish" (presumably unglazed) terra cottas. Among these, hydrofluoric acid was by far the most effective, "remov[ing] the

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[46] Weaver with Matero, 110.
[47] Charles U. Thrall, "Terra Cotta: Its Character and Construction—II," The *Brickbuilder* (1909) 18. 231.
[48] Joseph Timms, "Architectural Terra-Cotta," *The Brickbuilder* (1893), 2:1, 2.
[49] MacIntyre, 6.

dirt better than any cleaner tried." However, the surface finish was etched so badly that the use of the chemical as a cleaning agent was condemned.[50]

Between 1929 and the late 1970s, there is a paucity of published information regarding the cleaning of architectural terracotta. This may have been due to the political climate of the mid twentieth century; events such as the Depression, World War II, and the Korean war may have precluded research into the cleaning of architectural terra cotta and studies of historic building materials in general. The American middle class flight from cities and the new construction of the late 1940s and 1950s is symbolic of the fall of terra cotta from fashion; to serve the needs of the newly developing suburban communities, research emphasis was placed on the development of new building materials such as glass, plastics and vinyl. Commercial structures were constructed in the International Style, and the curtain walls that previously would have been terracotta tiles were constructed of glass instead. Preservation was a developing field during this era, and many preservation-minded endeavors were focused on organization, policy, and legislation.

In the late 1970s and early 1980s, masonry cleaning became a widely published subject in both Britain and the United States. At this point, the systematic notion that cleaning should be accomplished using the gentlest means possible began governing cleaning decisions. This new philosophy led to caveats against certain techniques, including those that had been practiced in recent decades. For example, sandblasting, a technique originally used for the removal of rust and scale from metals,

[50] "Cleaners for Terra Cotta," *National Bureau of Standards Technical News Bulletin* (1928), 131, 33.

had been adapted and used for cleaning masonry in the 1960s.[51] By 1982, the damage resulting from blasting was well documented. Many sources disparaged its effects and condemned its use.[52] Additionally, the "gentlest means possible" philosophy encouraged the use of "safer" chemical cleaning methods, resulting the rise of the commercial chemical cleaning industry in the United States in the 1960s and 1970s.

Since this early wave of publication, the techniques used in large scale cleaning of masonry (and specifically terra cotta) have changed very little. Knowledge of the effects of the techniques continues to grow, and a consensus exists regarding the appropriateness of certain techniques for various materials. Currently, three main categories of cleaning techniques are in wide-scale use: water based methods, mechanical and abrasive methods, and chemical methods.

Water Based Methods

The water based methods are largely agreed to be the much sought "gentlest means possible." These techniques for cleaning terra cotta are among the oldest, and unfortunately, among the least effective when used on their own. However, their efficiency improves when used in conjunction with other techniques. Water based methods include simple washing, high pressure washing, steam cleaning, and washing with a mild detergent.

Washing is enacted by spraying the masonry surface with special nozzles. The

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[51] John Ashurst, "Cleaning Stone and Brick," *Technical Pamphlet 4* (London: Society for the Protection of Ancient Buildings, 1977), 3.

nozzles are positioned on booms to allow for movement, ensuring even wetting of the façade. Usually, cold tap water is used for the washing process, although hot water may be more effective if the deposits are greasy.[53] This technique is intended to swell and loosen surface deposits and wash away all surface soiling. Spraying is often successful in achieving this result; tough surface deposits are loosened to a point where they can be removed in conjunction with mechanical methods, and surface soiling can be washed away.

The weaknesses of water cleaning are significant. Water alone, no matter the temperature, will never remove the chemically bound soiling commonly found on unglazed terra cotta. In addition, consistently spraying a structure with water creates the potential for saturating the building, a condition to which the building would never be exposed through the course of normal weathering. Potential hazards of saturating the building are well known. Water will penetrate every crack, crevasse, and mortar joint. The slightest defect in a joint may result in significant water penetration, causing the cramps used to secure the terracotta blocks to the frame to rust, resulting in dangerously unstable blocks. Timber members that would not otherwise be exposed to water may be dampened, creating conditions favorable to dry rot. Saturation of the masonry units themselves may lead to the efflorescence of migrating salts.[54]

Although initial responses were favorable, the use of high pressure water

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[52] Alan H. Spry, "Principles of Cleaning Masonry Buildings," *Technical Bulletin 3.1* (Melbourne, Australia: National Trust of Australia 1982), 18.
[53] Nicola Ashurst, *Cleaning Historic Buildings, vol.2.* (London: Donhead Publishing, 1994), 18.

washing has been discouraged since the mid 1980s. In 1977, the merits of the high pressure lance were delineated:

> The cutting action of the high pressure lance, using cold water, is useful in removing stubborn patches of dirt. It is a useful adjunct to both washing and blasting where it is used to freshen up the façade and clear it of dust.[55]

This practice was not advocated by conservators for long, however, and has since been strongly discouraged, acknowledging that high pressure water can damage masonry surfaces by etching or scarring.[56] In addition, the risk of saturation is greater, with high pressure washing driving water deep into the units and putting the structure at risk in freeze-thaw conditions.

The problem of saturation has been successfully controlled through the use of misting, which has been advocated since the 1970s. In this technique, a fine mist (nebulized water) is aimed at areas of soiling, allowing for the soiling to be softened using a minimal amount of water. This technique is sometimes modified so that a building is sprayed only intermittently, further reducing the chances of saturation, while the soiling is kept moist. Once the soiling is softened, it can be removed by a low pressure stream of water and, if necessary, scrubbing or scraping. Like washing, this technique can be very effective at removing surface soiling, but does not release chemically bound dirt.

Another water based technique that has enjoyed success in cleaning masonry is

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[54] Nicola Ashurst, *Cleaning Historic Buildings, vol. 2.* (London: Donhead Publishing, 1994), 21.
[55] John Ashurst, "Cleaning Stone and Brick," *Technical Pamphlet 4* (London: Society for the Protection of Ancient Buildings, 1977), 3.
[56] Anne Grimmer, *Keeping It Clean,* (Washington, DC: National Park Service, 1988), 15.

steam cleaning. In this technique, water is heated into steam and aimed at the surface using a low pressure nozzle. This technique is intended to swell hardened dirt and crusts that are then flushed from the surface with water or manually scraped away. Once used extensively, it has fallen out of vogue as a large scale method, possibly due to the increased efficacy of other techniques.[57] The advantages of steam cleaning remain, however. Unlike some other water based techniques, steam cleaning does not soak masonry, and is particularly useful in cleaning carved areas without causing mechanical damage. Unlike chemical methods, steam is not capable of depositing chemical residue. Steam is most effective against vegetation, and has had success combating greasy and tar-based soiling as well as heat-sensitive polymeric films.

Steam has disadvantages unique from other water based methods, however:

> Steam cleaning is not now favored because it is not particularly effective in removing dirt, is slow, generates large volumes of vapor which make the operation conspicuous, and can be dangerous to a careless operator.[58]

Ultimately, these disadvantages have led to a reduction in the use of this technique.

Washing with a mild detergent is frequently advocated as the most effective water based method. This technique involves lightly spraying the building with water before applying a non-ionic detergent and scrubbing gently to loosen and remove soiling. The building is then sprayed to remove the detergent and soiling.

Since the advent of non-ionic soaps, this method has been recognized as the least harmful method of cleaning unglazed architectural terra cotta that still produces a

[57] Grimmer, 14.
[58] Spry, 9.

significant improvement in appearance.[59] The non-ionic soaps do not leave an electric charge on the surface, and therefore will not attract dirt. Although there are risks associated with this method, they are very controllable: if detergents are properly washed away, the bacterial growth and increased surface hydrophilicity associated with detergent residue can be avoided. Ultimately, however, "no amount of detergent will help in stubborn areas of heavy, chemically-fixed soiling."[60]

In summary, water based methods, although they have associated risks, are the lowest risk technique for cleaning architectural terra cotta. With sufficiently gentle moisture and non-ionic detergent, the majority of soiling can usually be removed from the surface of the building without fully saturating the building or causing damage to the fireskin. Unfortunately, heavily soiled areas of chemically bound dirt will not respond to these methods, and other means of cleaning must be used.

Mechanical and Abrasive Methods

In an attempt to find a more effective cleaning system for chemically affixed dirt, mechanical and abrasive methods have been employed. These techniques include grinding as well as wet and dry blasting. In recent years, these methods have been widely condemned due to the irreparable damage they cause to the fireskin of fired clay materials.

The literature of the early 1980s indicates that carborundum discs were being used to "spin off" the outermost surface of masonry, thereby removing chemically

[59] Ashurst and Ashurst, 78.

bound soiling.[61] Unfortunately, unacceptable amounts of the surface itself were being removed with the dirt, resulting in a clean, uniform appearance of the building material. For terra cotta, the disastrous results were two-fold. Aside from producing an uncharacteristically uniform surface color and texture, the fireskin was removed, revealing the clay body which due to its more porous nature is more susceptible to natural weathering processes. Employing this method in a manner that would remove soiling without damaging the surface, however, is virtually impossible, and accordingly was condemned early on:

> Grinding wheels, pneumatic hammers and chisels, rotary teeth grinders and the like have no place on site for the cleaning of historic masonry and must not be used.[62]

Abrasive blasting, both wet and dry, works on a similar principle. Adapted for masonry cleaning in the 1960s, dry blasting was soon used on different varieties of stones in various states of deterioration. In the dry system, abrasive particles in a stream of compressed air are aimed at the masonry surface. The particles strike the surface, dislodging dirt adhering to the surface layer.[63] Unfortunately, the particles are unable to distinguish between soiling and substrate, and the masonry surface itself is attacked, sometimes dislodging particles to a depth of several millimeters. Wet blasting is the same technique as dry blasting with the addition of water, which is used to soften soiling and minimize resulting dust. The intended result of the systems is the

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[60] John Fidler, "Fragile Remains," 18.
[61] Spry, 17.
[62] *Annotated Master Specifications for the Cleaning and Repointing of Historic Masonry*. (Toronto: Ontario Ministry of Citizenship and Culture, 1985), 25.
[63] Nicola Ashurst, 32

same, however: to efficiently remove stubborn soiling.

Abrasive blasting has been praised for is speed and dramatic results. However, particularly in the case of architectural terra cotta, the dangers of abrasive blasting far outweigh the potential benefits. Due to the clouds of dust formed in dry blasting and the slurry produced in wet blasting, it can be very difficult for the operative to gage the success of soiling removal. Variations between masonry and mortar as well as variations in the units themselves are indistinguishable to the abrasive, and the operative must be relied upon to notice these differences. Misinterpretation of these variations can easily lead to overcleaning of the material and damage to the surface. In the case of terra cotta, overcleaning can result in irreparable damage and even full loss of the fireskin, the consequences of which are well documented. The technique therefore requires extremely skilled operatives, and resistance to the temptation to increase speed and pressure. Health risks for the operative have been associated with dry blasting as well. The clouds of dust formed as a result of the impact of sand on the masonry surface contain high volumes of silica. Prolonged exposure to this airborne silica has been associated with silicosis, a life-threatening lung disease. Wet abrasive blasting has additional disadvantages associated with wet techniques, such as penetration of mortar joints which results from the significant amounts of water necessary to remove the abrasive slurry from the building. Finally, both techniques are noisy and messy, and can cause severe disruption to life in and around the building in question.

There have been several attempts to reduce the damage caused by blasting

techniques. For example, many different substances have been use as abrasives. Crushed walnut shells, de-oiled cornhusks, and glass beads have all been used in an effort to soften the impact of the abrasive, but none of these have been shown to significantly affect the potential for damage on unglazed terra cotta. Microblasting is a technique that has been advocated as less damaging to masonry. This is essentially a dry abrasive method that employs small, rounded particles as abrasives. These particles are projected at the surface at much lower pressures using a pencil-like gun, affording the operative much greater control of the process. Efforts to establish the suitability of small-particle abrasive techniques for unglazed architectural terracotta have not yet been successful, however.[64] In fact, micro-blasting tests in the Architectural Conservation Lab at the University of Pennsylvania have revealed that glass powder with 20-40 micron particles and dolomite removed the fireskin of unglazed terracotta at low psi, an indication of the unsuitability of this technique.[65]

Laser Cleaning

Another technique that has garnered attention in the world of masonry is laser cleaning. As early as 1975, laser cleaning was used to remove gypsum crusts from marble.[66] However, the application of this technique to unglazed architectural terra cotta was not published until 1996.[67] The technique demonstrated in this study used a

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[64] Nicola Ashurst, 40.
[65] Frank G. Matero, personal communication.
[66] Spry, 8.
[67] John Larson and Martin Cooper, "The Use of Laser Energy for Cleaning Architectural Terracotta Decoration," in *Architectural Ceramics*, ed. Jeanne Marie Teutonico.

Q-switched Nd:YAG laser, which was adjusted to a wavelength that targeted the soiling, and aimed at areas of soiling on a piece of architectural terra cotta.[68] Through a number of thermo-mechanical mechanisms, the laser removed dirt form the surface of the terra cotta.

Laser cleaning has distinct advantages. The laser is monochromatic, allowing the operative to choose a single wavelength that will interact only with the soiling and not the surface of the terra cotta. As only short pulses are needed, absorption of large quantities of heat can be prevented. This technique allows tremendous precision, and has been used successfully in fine arts conservation for several years.

As with any cleaning mechanism, however, there are possible disadvantages to laser cleaning. If the laser is not properly adjusted, it can cause surface pitting, demonstrating the need for a skilled operative. The technique is slow, adding to the expense of the project, and has yet to be tested on a large scale building. The long range effects of the technique, both for the building and the operative, are unknown. Before this technique can be commonly specified, more information and study are required.

Chemical Cleaning Methods

Chemical methods have been used to clean unglazed architectural terra cotta since at least the 1920s. Both alkaline and acidic cleaners have been employed over the years in an attempt to remove stubborn soiling from the surface. Despite the

[68] Ibid, 98.

damaging salts that are often left behind, chemical methods are frequently employed in cleaning severely soiled unglazed architectural terra cotta.

The most commonly used alkaline cleaners include sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH). In employing these cleaners, the surface of the building is first rinsed with water, filling the pores and capillaries in an attempt to prevent the cleaner from penetrating the masonry. The chemical is then applied, remains on the surface for the allotted dwell time, and is rinsed thoroughly. Often, the cleaner is neutralized with an acidic after-bath, and thoroughly rinsed again. Thorough rinsing is an essential part of the process, particularly after the application of the neutralizing agent, as neutralization results in the formation of salts that have the potential to damage the masonry.

Alkaline cleaners are used more frequently on glazed terra cotta than unglazed, but have been employed as a pre-wash for unglazed terra cotta. These cleaners are lauded for their effectiveness against greasy dirt, particularly when combined with surfactants. However, the disadvantage of using alkali-based cleaners is widely understood by professionals: the risk of staining white efflorescence is extremely high. Sodium hydroxide has the tendency to penetrate and remain in the pores and capillaries of the body of the terra cotta, causing destructive subflorescence which will in turn cause total breakdown of the terra cotta surface.[69] These effects have been somewhat less pronounced in potassium hydroxide and ammonium hydroxide based

[69] Weaver with Matero, 124.

cleaners.[70]

The most commonly used chemical solutions for cleaning unglazed architectural terracotta are acidic cleaners. For unglazed architectural terra cotta, hydrofluoric acid based cleaners are preferred.[71] As with any chemical cleaning system, the surface to be cleaned is thoroughly pre-wet. The proprietary cleaner is then applied to the surface where it remains for the allotted dwell time (usually two to five minutes) before being washed away. The surface is then thoroughly flushed with water. The hydrofluoric acid based cleaner attacks the complex silicates of the fireskin surface, dissolving the uppermost surface of the fireskin, thereby releasing not only the chemically bound soiling but a layer of the surface as well.

Despite the inherently destructive nature of this system, it is still widely used and is generally considered to be the most effective way to remove unsightly, difficult to remove dirt. The most common method of evaluating the success of cleaning is through visual examination; when judged by this standard, this technique is deemed highly effective. Unlike other chemical cleaners (both alkali- and acid-based products), hydrofluoric acid based cleaners do not deposit soluble salts on the masonry surface. Additionally, when used properly, hydrofluoric acid based cleaners achieve a level of cleanliness that is not attainable through any other method without significant

[70] Grimmer, 18.
[71] Hydrofluoric acid based cleaner have also been advocated for cleaning brick, which introduces a separate but significant set of issues. Bricks vary widely in composition and texture, and will accordingly be affected differently by the cleaner. Additionally, mortar joints between bricks are more prevalent and generally larger than the corresponding joints between terra cotta units. This creates a problem for the acid soluble mortar, and can result in dissolution of the mortar, and streaking and staining. See page 104 of Volume One of Nicola Ashurst's *Cleaning Historic Buildings* for further discussion.

damage to the material.

The system is not without its disadvantages, however. HF is extremely corrosive, and represents a danger to the operative, passers-by, the adjacent properties, and any organic life form it touches. Due to its corrosive nature, most surfaces will be etched by the cleaner, requiring comprehensive sealing and masking of all non-masonry surfaces. While it does not deposit soluble salts, it can deposit insoluble salts such as calcium fluoride and magnesium fluoride. If the cleaner is allowed to trickle from upper levels of the building onto lower levels, streakiness and staining invariably occur, most notably seen on the face of the Natural History Museum in London, cleaned in the 1970s. As with many cleaning systems, if used improperly, the cleaner represents a significant danger to the operative and building itself.

Throughout the twentieth century, many different cleaning systems have been employed in an attempt to remove the stubborn soiling that attacks unglazed architectural terra cotta. While there is professional consensus that the gentlest means possible should always be used, it is also understood that the gentlest methods sometimes do not achieve the level of cleaning desired.

> There seems to be an international consensus among conservators, architects, building maintenance surveyors and the terracotta manufacturers themselves that a combination of hand-scrubbing with stiff nylon brushes and a minimum of water washing, with the option of using a neutral organic detergent, seems to be the most conservative approach and least harmful to the glazes and fireskins of the material. However, it has to be acknowledged that these detergents do not give the most effective clean.[72]

In the quest for the most effective cleaning process, hydrofluoric acid based

cleaners, used responsibly, have become the preferred method to clean. While the dangers of using hydrofluoric acid based cleaners have been known since their earliest use, when compared to other effective methods (namely abrasive and alkali-based cleaners) these cleaners are perceived as the most effective and least damaging way to remove chemically bound soiling from unglazed terra cotta. This thesis will attempt to determine the level of damage caused by HF based cleaners, and the significance of that damage to the eventual behavior and durability of the cleaned material.

[72] John Fidler, "Fragile Remains," in *Architectural Ceramics*, 19.

Chapter Four: Methodology

As previously stated, this thesis has two distinct goals: to describe and quantify the changes to the surface pore structure of architectural terra cotta caused by hydrofluoric acid based cleaners, and to assess the impact that these physical changes have on the material. This two-fold approach has led to two distinct methodologies.

Except for the use of mercury intrusion porosimetry in the study conducted by Ashurst, Woolfit, and Forshaw, quantification of the changes to the fireskin surface caused by hydrofluoric acid based cleaners had not been attempted previously. Several methods of quantification were investigated. These methods fell into two distinct categories: techniques based on assessment of surface roughness, and techniques based on measurement of magnified surfaces. Complete explanations of each method are found later in this chapter.

To assess the impact of the physical changes to the fireskin surface, it was necessary to design and implement a series of tests to simulate the damage caused by natural weathering processes. These tests included standard procedures for salt crystallization, freeze thaw testing, and exposure to UV light and condensation in an accelerated weathering chamber. The exact methodology followed for the simulated weathering tests will be discussed in this chapter.

Before either quantifying or assessing physical changes caused by hydrofluoric acid based cleaners, it was first necessary to characterize the material. Determining the essential properties and characteristics of a material is an integral part of any study or experiment; the resulting understanding of the components and attributes of a

material allows a conservator to make informed decisions regarding treatments. Samples subjected to various cleaning regimes were characterized using several methods, including reflected and transmitted light microscopy, as well as instrumental analytical techniques. Procedures for the characterization techniques employed will be discussed later in the chapter.

Sample Acquisition

Samples were obtained from two modern producers of architectural terra cotta. Fifty 4" by 4" by 1" tiles were donated by Gladding McBean of Lincoln, California. Now a division of Pacific Coast Building Products, Gladding McBean has produced terra cotta continuously since 1875. Fifty 6" by 6" by ¾" tiles were purchased from Boston Valley Terra Cotta of Orchard Park, New York. Boston Valley has produced terra cotta since 1981. All samples were unsoiled, and in pristine condition. Unsoiled samples were deliberately selected with the expectation that a lack of soiling would increase the visibility of the interaction between the cleaner and the substrate.

Sample Preparation

Sample preparation was a multi-step process. The large samples were cut into smaller samples using a table saw with a masonry blade. Each 4" by 4" by 1" tile was cut into four 2" by 2" by 1" samples, and each 6" by 6" by ¾" tile was cut into four 3" by 3" by ¾" samples. These smaller samples were then carefully labeled using indelible ink. All phases of multi-phased samples originated from the same tile; for

example, BV-04-0, BV-04-1, BV-04-2, and BV-04-3 were all cut from the same 6" by 6" tile.

Samples were given a number consisting of two or three letters indicating the manufacturer, a number naming the sample, and a number indicating how many times the sample should be treated with the cleaning solution. For example, sample BV-03-3 was made by Boston Valley Terra Cotta, and was washed with the cleaning solution three times. A sampling summary is included as Appendix E.

The second step of the preparation process was cleaning the samples with a hydrofluoric acid based cleaner. SureKlean™ Restoration Cleaner manufactured by ProSoCo of Kansas City was selected for its ready availability, common field use, and affordability. While hydrofluoric acid is the most commonly cited component, other compounds including hydroxyacetic and phosphoric acids are also components of the solution. Care was taken to ensure that the samples were washed with the cleaner according to the manufacturer's instructions.[73]

The cleaner was diluted by equal parts cleaner and water, which is the maximum recommended concentration. Each tile was thoroughly wet with water, and the diluted cleaning solution was applied using a stiff bristled nylon brush. The cleaning solution was allowed to dwell on the surface of the tiles for five minutes; again, acceptable according to the manufacturer's instructions. At the end of the dwell period, the cleaning solution was rinsed away, and reapplied. The surface was lightly scrubbed with the application brush, and rinsed again. The samples were then flushed

under a tap at full strength for five minutes, and allowed to dry for at least twenty-four hours. This process was then repeated for samples that were designated for multiple washes.

The final step of sample preparation was to seal the sides of the samples. As the tests conducted were concerned with the fireskin surface only, it was necessary to prevent water infiltration into the more porous inner body of the tiles. This was achieved by sealing the sides of each sample with a clear epoxy resin, in this case Devcon's PolyStrate 2-Ton Crystal Clear Epoxy. The epoxy was allowed to cure for 24 hours before subjecting the samples to the test procedures.

CHARACTERIZATION

After the samples were prepared, they were characterized using several methods: reflected light microscopy, polarized light microscopy, x-ray diffraction, scanning electron microscopy, and a water absorption immersion test.

A Nikon Microflex AFX-II microscope was used to visually characterize the samples. The samples were examined using reflected light under 40X and 100X. Scanning Electron Microscopy (SEM) was used to evaluate the condition of the surface of the samples. One set of samples of each type of terra cotta were evaluated. The samples were prepared for the microscope in a Polaron Instruments E5000 SEM coating unit, which coated the samples with a fine layer of gold. The samples were then viewed using a JEOL JSM 6400 Scanning Electron Microscope. The Boston

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[73] The manufacturer's instructions are included as Appendix G.

Valley samples were examined under magnifications of 650X and 2000X, while the Gladding McBean samples were examined under magnifications of 1000X and 3000X. A concerted effort was made to take photomicrographs of areas that were representative of the sample as a whole. The photomicrographs and descriptive analysis of the SEM observations can be found in Chapter Five.

A mineralogical characterization of the terracotta was performed using two different methods. Thin sections of the samples were examined under transmitted polarized light with a Nikon Microflex AFX-II microscope at magnifications of 40x and 100x. X-Ray Diffraction (XRD) was used to identify mineral constituents of the samples that were not readily identifiable using polarized light microscopy. The samples were ground into a powder and mounted in the sample holder. The sample was evaluated using a Rigaku Geigerflex apparatus. Both samples were run under conditions of 2°-60° at 2° per minute.

The surface porosity of the samples was determined using the ASTM standard method C67-97 for water absorption through cold water immersion.[74] The samples were dried in a ventilated oven at 100°C for 24 hours, allowed to cool in a desiccator to a constant weight, and their weights were recorded. They were then immersed in de-ionized water for 24 hours. Upon removal, excess water was blotted from the surface of the sample with a damp cloth, and the samples were weighed. The percent water absorption was calculated using the following formula:

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[74] Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, ASTM Designation C 67-97.

$$Absorption,\% = \frac{100(W_s - W_d)}{W_d}$$

where W_s = saturated weight of the specimen, and
where W_d = dry weight of the specimen

Results of all characterization procedures can be found in Chapter Five.

Quantification of Change

Several methods of quantifying change to the physical structure of the fireskin surface caused by the hydrofluoric acid based cleaner were investigated. These changes could be quantified by assessing the differences of surface texture of the samples, by measuring the visible physical changes to the surface at a microscopic level, or by performing laboratory tests. To assess surface roughness, laser triangulation profilometry and a human touch test were investigated. Measurement of visible physical changes included measurement of scanning electron micrographs of the fireskin surface with a Carl Zeiss Zidas machine. Laboratory tests included water vapor transmission and water drop permeability.

In laser triangulation profilometry, rubber replicas of the surface are analyzed, avoiding the color bias that would result from the assessment of the actual surface itself. In this process,

> [t]he instrument projects a beam of light perpendicular to the specimen's surface. The light triangulates the surface position by imaging the laser spot with an adjacent lens to a position sensitive detector. [A computer is] used to digitize the signal, control the stage's

positioning, and process the surface profile.[75]

Although this technique has been used with success to assess the surface roughness of building materials, it does so at considerable expense and difficulty. Accordingly, it was determined that laser triangulation profilometry was not the most efficient way to assess the surface roughness of the samples.[76]

Assessment of surface roughness by human touch was also explored. A pre-test was conducted to ensure that human touch was sensitive enough to detect the differences in surface roughness of these samples, and that the participants were able to create a hierarchy of roughness. Once this was determined, a method for assessing changes to the surface was developed by the author. Ten participants were given four sets of samples, two of each type of terracotta (GMB-02, GMB-03, BV-02, and BV-03). The samples were placed face side up, thereby concealing the sample number. The subjects were asked to feel the washed fireskin surface of the samples, and rank them in order from roughest to smoothest. Results of this test are found in Chapter Five.

The possibility of measuring of changes visible under the scanning electron microscope was thoroughly explored. Since samples examined in the scanning electron microscope must be coated with either gold or carbon, the technique introduces error. The coating process is irreversible, and permanently alters the

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[75] A.E. Charola, Carol Grissom, Evin Erder, Melvin J. Wachowiak, and Douglas Oursler, "Measuring Surface Roughness: Three Techniques." In *Proceedings of the Eighth International Congress on Deterioration and Conservation of Stone.* (Berlin, 30 September–4 October, 1996, 1421-1434), 1423.
[76] Conversation with A. E. Charola regarding unpublished results of the surface roughness assessment study.

sample. This precludes the examination of a single sample at various stages of the cleaning process, since it would be impossible to examine a single sample before washing and then after each successive stage of washing. It was therefore necessary to examine sets of samples. All samples in a set were cut from the same tile, and the author was required to make the assumption that the porosimetry of the surface of each set of samples was virtually identical prior to treatment. Three sets of samples of each type of terracotta were examined under the scanning electron microscope. The anticipated procedure was to take micrographs of three representative areas of each sample, then measure pore diameter of all visible pores in these areas using a Carl Zeiss Zidas machine. This tool is essentially a computerized ruler; using an electronic mouse, the operative traces the surface features as seen in the scanning electron micrograph. The Zidas immediately prints out the surface area of the traced feature. From this printout, it is possible to calculate the pore size distribution of each sample. By comparing the pore size distribution of unwashed, once washed, twice washed, and thrice washed samples, the changes caused by the cleaning solution should be noticeable.

However, it was impossible to measure the pores of the surface with the Zidas as originally anticipated. When evaluated at magnification sufficient to see the pores, it was not possible to get an adequate statistical sample of pores to measure. At a magnification satisfactory to see a pore, only a single pore was visible within the field of view. It was therefore necessary to amend the quantification procedure. Rather than measure the size of the pores and compare the relative pore size distribution, a

7,762 square micrometer area of the surface was evaluated. The total surface area encompassed by pores (either one large pore or several smaller pores) was compared to the total intact surface area. Three micrographs each were taken from an unwashed and a thrice washed sample of each type of terracotta. The areas photographed are not representative of the surface as whole, but rather are areas that had a significant number of pores visible. A concerted effort was made to photograph areas that were similar from sample to sample. The results of the analysis are discussed in Chapter Five.

An amended ASTM standard for water vapor transmission[77] was performed on the unwashed and thrice washed samples. It was necessary to amend the standard due to space and laboratory material constraints. The test specimens were prepared by cutting them into 4" by 4" squares, which were then nestled into plastic containers filled with water. The water level came within 1" of the tile. A water-tight seal was created around the edge of the sample using backer rod and paraffin wax. Each specimen was weighed and the weight recorded before being placed into a desiccation chamber. The relative humidity of the chamber was maintained below 50% through the use of anhydrous calcium sulfate. The average RH of the chamber was approximately 23%. The samples were weighed on a daily basis. The water vapor transmission rate was calculated using the following formula:

[77] Standard Test Methods for Water Vapor Transmission of Materials. ASTM Designation E 96-95.

$$WVT = \frac{G}{tA} = \frac{(G / t)}{A}$$

where *WVT*= rate of water vapor transmission,
G = weight change (from the straight line) in grams,
t = time in hours,
G/t = slope of the straight line in grams/hour, and
A = test area

The permeance of the samples was then calculated using the following formula:

$$Permeance = \frac{WVT}{S(R_1 - R_2)}$$

where WVT = rate of water vapor transmission,
S = saturation vapor pressure at test temperature (mm Hg)
R_1 = relative humidity at the source
R_2 = relative humidity at the vapor sink.

Results of the experiment are discussed in Chapter Five, and the table of results can be found in Appendix B.

In a final attempt to quantify the changes of the properties of the material as a result of treatment with the cleaning solution, a simple laboratory test was performed. A water drop absorption test based on the Rilem Test number II.8a/b was performed in an attempt to assess changes in hydrophilicity of the fireskin surface from sample to sample. Using a burette filled with de-ionized water, a 0.5 ml drop of water was dropped onto the surface of each sample from a distance of 1 cm, and the amount of time elapsed before absorption of the water drop was measured. Full absorption was defined as the point at which the area encompassed by the water droplet no longer appeared reflective in raking light. The water absorption was then calculated using the

formula:

$$\%WaterAbsorption = \left(1 - \frac{t_x - t_n}{t_x}\right)100$$

Where t_x = absorption time into the washed surface, and
t_n = absorption time into the unwashed surface.

Results can be found in Chapter Five, and full data sets can be found in Appendix B.

Testing Program

A series of three tests were designed to simulate weathering and expose the samples to weather related conditions. Salt crystallization and freeze/thaw tests were employed to simulate isolated conditions, and an accelerated weathering chamber was used to expose the samples to cycles of ultraviolet light and condensation. For each of the tests, pre-tests were run to gauge the severity of the tests, and ensure that the tests would be informative rather than simply destructive. One unwashed sample and one thrice washed sample of each type of terracotta were exposed to the tests. Testing of full sets of samples ensued. The procedure for each test follows.

Salt Crystallization

The salt crystallization test employed is based on the Building Research Establishment's crystallization test for limestone.[78] As directed by the standard, a solution of sodium sulfate decahydrate was prepared. The pre-dried, pre-weighed samples were submerged in individual containers of the solution for two hours. The

samples were then removed from the solution, and dried in a ventilated oven for sixteen hours at 100 ± 2°. The samples were removed from the oven and allowed to rest for six hours before returning to the sodium sulfate decahydrate solution. This cycle was repeated twenty-one times; although this exceeds the recommendations of the standard by one week, the results of the pre-tested samples indicated that fourteen cycles were inadequate to produce significant results.

The samples were allowed to cool to a constant weight, and then weighed. The percentage weight loss was then calculated using the following formula:

$$\%\ weightloss = 100 \left(\frac{W_f - W_1}{W_1} \right)$$

Where W_f = the final weight of the samples after testing, and
W_1 = the original weight of the samples.

The results of this test can be found in Chapter Five.

Accelerated Weathering

The third set of samples was subjected to the cycles of an accelerated weathering chamber. The test was run in accordance with ASTM standard G 53-88.[79] The samples were prepared as discussed above, then secured with aluminum clips to the aluminum sample holders. Each sample beginning with the prefix "BV" was attached to its own sample holder. Each sample with the prefix "GMB" was randomly

[78] K.D Ross and R.N. Butlin, *Durability Tests for Building Stone.* (Watford: Building Research Establishment, 1989.), 14.
[79] Standard Practice for Operating Light- and Water- Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials. ASTM Designation G 53-88.

paired with another "GMB" sample, and attached to a sample holder. This arrangement was mandated by space and size constraints.

The sample holders were then placed in the accelerated weathering chamber, a QUV SE/SO Accelerated Weathering Tester with solar irradiance control and spray option. The conditions were set for four hours of ultraviolet light at 60°C, alternating with four hours of condensation at 40°C. Although the recommendation of the standard is four hours of condensation at 50°C, equipment restrictions mandated the 40°C condensation temperature.

The testing period chosen was 504 hours, or three weeks. In accordance with the standard, the samples were rotated horizontally on a daily basis, and vertically halfway through the test. Upon removal from the chamber, the samples were weighed, and their weights recorded. The percentage weight loss was calculated using the following formula:

$$\%\ weightloss = 100\left(\frac{W_1 - W_2}{W_1}\right)$$

where W_1 = the original weight of the sample, and
W_2 = the post-testing weight of the sample.

Results can be found in Chapter Five, and all relevant data in Appendix A.

Freeze/Thaw

A modified version of the ASTM standard C 67-97[80] freeze/thaw test was

[80] Standard Methods for Sampling and Testing Brick and Structural Clay Tile, ASTM Designation C 67-97.

conducted on six sets of samples that were prepared as discussed above. The samples were dried, allowed to cool to a constant weight, and their weights were recorded. The samples were carefully examined, and any cracks or disruptions in the surface were marked with indelible ink. The samples were placed treated face down onto a layer of glass rods in metal trays. The trays were then submerged in the thawing tank, a large plastic tank filled with enough water to cover all three trays of samples. The water of the thawing tank was maintained at 24°C, ± 2°. After soaking for four hours, the majority of water was drained from the trays, leaving enough water to submerge the samples to half their height. The samples were placed in the freezing chamber, a Kenmore freezer, model number 25221, with the temperature maintained at -15°C. The samples remained in the freezing chamber for twenty hours before returning to the thawing tank. Fifty 24 hour cycles were completed. At the end of the fifty cycles, the samples were dried to a constant weight and their weights recorded. Percentage weight loss was calculated using the following formula:

$$\% \ weightloss = 100 \left(\frac{W_1 - W_2}{W_1} \right)$$

where W_1 = the original weight of the sample, and
W_2 = the post-testing weight of the sample.

The results of the test can be found in Chapter Five, and all related data in Appendix A.

Chapter Five: Results and Discussion

The results and discussion of the characterization, quantification, and weathering tests are found below. Full sets of data for each of the tests can be found in Appendices A, B, C, and D.

Characterization

At least one sample of each type of terracotta was characterized in each test. It was assumed that all samples are acceptably uniform in character and composition to have one representative sample for each type of terracotta.

Reflected Light Microscopy

Samples were examined under magnifications of 40X and 100X, and photographed at the same magnification.

Sample Number	Description
BV-01-0	The sample is buff with gray undertones (Munsell color designation was 2.5Y 8.5/2) with some areas of golden discoloration. Two tiers of inclusions are visible: small particles of grog ground to a size compatible with the clay particles for thorough mixing, and larger inclusions which are both larger fragments of grog and random fibrous inclusions. Smaller inclusions are of both high and low sphericity, all sub-rounded in shape. Although varied in color, brick red and black particles predominate. Larger inclusions of grog are of high sphericity, and angular. Large, fibrous inclusions are of

	very low sphericity. Inclusions of all sizes and shapes are distributed evenly throughout the sample. The texture is relatively rough, with gently sloping peaks and valleys. A lattice work of peaks creates a mountainous superstructure on the surface of the sample.
BV-01-1	Sample is identical in color and inclusions to the unwashed sample, and general differences in the texture of surface of the sample cannot readily be distinguished optically. The relief of the superstructure is significantly lower than on the previous sample.
BV-01-2	Inclusions of the samples are identical to those described above, but the basic color has become a shade darker (2.5 Y 9/2). Again, textural changes to the general surface are too insignificant to discern optically, but the high relief of the superstructure has been reduced, and the sharp peaks have dulled into gentle hills.
BV-01-3	Inclusions remain identical, and basic color remains at 2.5 Y 9/2. The superstructure is no longer distinct; it simply appears to be normal surface variation.
GMB-01-0	The sample is bright golden yellow in color (Munsell designation 2.5 Y 8/6), with subtle variations in color that reveal the heterogeneous composition of the material below; it appears that a semi-translucent yellow layer is concealing color and textural variations below. Surface texture is rough, with easily discernable peaks and valleys. There are two major categories of inclusions: brick red grog, and semi-opaque milky-white quartz. Both types of inclusions vary in size, shape, and sphericity. Grog typically ranges from well rounded particles with high sphericity to sub-angular particles with low

	sphericity. The variation is more subtle with the quartz particles, which range from highly angular spherical particles to angular particles with low sphericity.
GMB-01-1	The sample appears identical to the unwashed sample in color, texture, and character of the inclusions.
GMB-01-2	The sample appears identical to the unwashed sample in color, texture, and character of inclusions.
GMB-01-3	The texture and character of the inclusions remains unchanged from the unwashed sample. However, the background color appears lighter than the other samples (2.5 Y 8.5/6).

Essentially, the surfaces of the samples do not appear markedly changed under reflected light. Minor variations in texture and color are noticeable, however. Textural changes are assumed to be the result of the silicate dissolution that is characteristic of the HF + SiO_2 reaction. The color changes in the Boston Valley samples are also a likely result of this chemical reaction. The lightening of tone observed in the Gladding McBean samples may result from similar changes to the surface, or may result from the deposition of insoluble salts or colloidal silica. The phenomenon of staining white bloom is widely discussed in conservation literature:

> Products of this reaction are silicofluorides and insoluble colloidal silica.....Many glazed surfaces have been etched and the white deposition of colloidal silica either as bloom or in drips are clear indications of where the method has been used.[81]

[81] Ashurst and Ashurst, 77.

The most prominent and frequently discussed example of this type of staining is the Natural History Museum in London.

Scanning Electron Microscopy

One set of samples of each type of terra cotta was evaluated under the scanning electron microscope. The resulting photographs can be seen in Appendix D.

Sample Number	Description
BV-01-0	The latticework of peaks visible under reflected light is visible at 650X, but very few pores are visible at this magnification. There is significant surface variation, with distinct peaks and valleys. Platelet shapes are visible. At 2000X, an occasional large pore is visible.
BV-01-1	The surface appears very similar to the unwashed sample, but the latticework of peaks is no longer distinct. At 2000X, a few small pores are visible.
BV-01-2	The texture of the surface appears virtually identical to that of BV-01-1. However, increasing numbers of small pores are visible. These pores are long and irregular in shape, and are molded along the edges of the platelet shapes.
BV-01-3	The relief of the surface has again decreased. Irregularly shaped small pores are visible, but in smaller numbers than on the twice washed samples. At 2000X, miniscule holes are visible (less than 1 micron in diameter), giving the surface an almost spongy appearance.
GMB-01-0	The surface of the sample has significant relief, with sharp-edged peaks and visible valleys. At 1000X, clusters of small pores are visible, as are larger, oblong pores. At 3000X, the

	pores simply appear larger; increased numbers of pores are not visible.
GMB-01-1	The variations in the surface texture are greatly reduced on this sample, but significant changes to the pore size or structure are not visible, even at 3000X.
GMB-01-2	Variations in the surface texture have again reduced: the sharp edges of the peaks have been smoothed away entirely. Increased numbers of clusters of perforations (diameters ranging from ½ to 1 micron) are visible. At higher magnification, the shape of these pores is more clearly oblong.
GMB-01-3	Variations in surface texture have been reduced again, with the surface of this sample appearing almost smooth. Although there are pore clusters, the pores are neither as large nor as concentrated as in the twice washed sample. This is confirmed at higher magnification.

The texture of the surface of the Boston Valley terracotta samples was visibly altered as a result of the treatment. A significant increase in the number of visible pores occurs between the first and second washings, but this number declines again after the third washing. Also of interest are the perforations that become visible under high magnification. These perforations are most likely the result of the interaction between the hydrofluoric acid and the silicate layers of the clay, while the alumina layers are left intact.

While the surface texture of the Gladding McBean samples changed distinctly, changes in the number of pores are not as dramatic. Like the Boston Valley samples, the greatest number of pores are visible after the second washing, but the quantity

declines again after the third washing. In theory, this could be the result of the deposition of silicofluorides, but surface contamination is not visible in the scanning electron micrographs.

POLARIZED LIGHT MICROSCOPY

Four samples of terra cotta were evaluated in thin section: one unwashed and one thrice washed Boston Valley sample, and one unwashed and one thrice washed Gladding McBean sample. The samples were examined in transmitted and polarized light.

BOSTON VALLEY UNWASHED	In transmitted light, the matrix is olive buff in color and appears to be composed of very fine particles. Embedded in the matrix are inclusions of widely varied shape, size, and cleavage. Color varies within the color families of brown, buff, and off white. In polarized light, it is apparent that many of the inclusions are in fact pores. Approximately 30 percent of the non-matrix area consists of pores: about half of these are quite large, while the other half are tiny and scattered throughout the sample. Some quartz is visible, but the primary non-matrix, non-pore component of the sample is not easily identifiable. It has well defined cleavage, appears bright in polarized light, and has a uniaxial negative interference figure.
BOSTON VALLEY THRICE WASHED	This sample appears very similar in transmitted light to the untreated sample. The color of the matrix is richer, but this is most likely the result of a very slight difference in thickness of the thin section, a variation caused during preparation. In

	polarized light, the sample again appears very similar to the untreated sample. No changes are noticeable.
GLADDING McBEAN UNWASHED	In transmitted light, the matrix is mustard brown in color and appears to be composed of very fine particles. Again, embedded in the matrix are particles varying widely in shape and size. There is greater variation in color of the inclusions; while most are in the brown/buff family, there a few black inclusions. Long, colorless lenses swirl through the matrix and inclusions. In polarized light, these lenses no longer appear clear but gray: discovery of a uniaxial positive interference figure confirms the presence of quartz. The inclusions that appeared black in transmitted light appear a deep, brick red in polarized light. Within each of these red inclusions, many smaller, grayish inclusions are visible. It is likely that these reddish particles are grog, and the inclusions bits of quartz that were mixed with the clays in the first firing of the grog. This sample does not appear to be very porous; only very fine pores are visible, and these are not prevalent.
GLADDING McBEAN THRICE WASHED	The treated sample appears very similar to the untreated sample. Like the Boston Valley samples, there is a difference of color of the matrix of the two samples. However, the matrix of the treated sample appears less rich in this sample, confirming the hypothesis that the variation in color is due to preparation of the thin section rather than treatment. There are no notable differences between the treated and untreated samples.

At this low magnification, it is not possible to see changes caused by treatment

with the cleaning solution. However, the formation of quartz lenses visible in the Gladding McBean terracotta indicates that the quartz was not mixed completely into the slurry during the manufacturing process. The fine particles of clay were not sufficiently separated to fully surround the quartz grains. In combination with the circular motion of the mixer, rounded lenses of quartz were formed.

X-Ray Diffraction

One sample of each type of terracotta was evaluated using x-ray diffraction. The results of each are shown below and in the graphs in Appendix C. The primary components of the Boston Valley terracotta identified by XRD were mullite, indialite, kyanite, and quartz. The primary components of Gladding McBean identified by XRD were mullite, quartz, and aluminum phosphate.

The two prevalent crystalline structures common to the two terracottas were mullite ($Al_6Si_2O_{13}$), and quartz (SiO_2). Kyanite and aluminum phosphate were also found in both types of terracotta, although each was prominent in one type and trace in another. As would be expected, with the exception of aluminum phosphate, all of these components are various types of silicates. Silicates compose the majority of the earth's crust, and are frequently the basis of building materials.[82] The unit cell of all silicates is the tetrahedron; silicates are classified according to the preferred bonding structure of these tetrahedra to each other.

Mullite was a principal component of both types of terracotta. Mullite is

classified as a nesosilicate, meaning that two silicate tetrahedra bond to each other by bonding with the same cation, in this case, aluminum. Mullite, a species similar to sillimanite, is rare in the natural world, but is a common product of artificial Al_2O_3-SiO_2 systems at high temperature.[83] It is logical to assume that mullite was formed during the firing process.

Quartz is a common component of both terracottas. Quartz is classified as a tectosilicate, indicating that the tetrahedra bond to form a complex latticework of molecules. Quartz has several polymorphs, and past XRD study has revealed coesite as a component of terracotta.[84] The crystalline structure identified in both the Boston Valley and Gladding McBean terracotta was identified simply as quartz rather than any of the polymorphs. The concurrent presence of non-polymorph quartz and minerals that require high temperature and pressure to form is explained by the stability diagrams for each substance. It is possible for both kyanite and mullite to form at lower pressures/temperatures than are necessary for the formation of the quartz polymorphs.

Kyanite (Al_2SiO_5) is another distinctive component of the Boston Valley terracotta. Like mullite, it is classified as a nesosilicate. It is most stable at high temperatures and pressures.[85] It is likely that the formation of kyanite was the result of the extreme temperatures reached during the firing process.

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[82] Cornelis Klein and Cornelius S. Hurlbut. *Manual of Mineralogy, 23rd edition.* (New York: John Wiley and Sons, 1993), 440.
[83] Ibid, 456.
[84] Moynehan, 63.
[85] Klein and Hurlbut, 455-6.

The previously unidentified distinguishing component of Boston Valley terracotta is indialite ($Mg_2Al_4Si_5O_{18}$). A high-temperature polymorph of cordierite, indialite is classified as a cyclosilicate, meaning that the silicate tetrahedra bond in ring formations. Again, high temperatures that are necessary for the formation of indialite are the result of the firing process.

Gladding McBean terracotta was shown to be composed primarily of three major mineral constituents: mullite, quartz, and aluminum phosphate ($AlPO_4$). Aluminum phosphate, although not defined as a specific mineral, is a component of several minerals in the apatite mineral group. This is the only component of the terracotta that is not some form of silicate.

The presence of silicates is of tremendous importance to this study, since it is well documented that hydrofluoric acid attacks silicates indiscriminately.[86] As previously discussed, this is the mechanism by which HF based cleaners are effective. The silicate rich mineral composition of both types of terracotta studied make them excellent candidates for successful cleaning treatment using a hydrofluoric acid based cleaner, and physical changes to the surface are to be expected.

POROSITY

The ASTM standard test for cold water absorption[87] was used to determine the surface porosity of the samples. Samples GMB-02, GMB-03, BV-02, and BV-03

[86] Nicola Ashurst, 69.
[87] Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, Designation C67-97.

were all used for the test. The results are summarized in the chart below:

Sample Number	Percent Absorbed
BV-02-0	6.97%
BV-02-1	6.62%
BV-02-2	6.71%
BV-02-3	6.59%

Sample Number	Percent Absorbed
BV-03-0	6.80%
BV-03-1	6.55%
BV-03-2	6.55%
BV-03-3	6.60%

Sample Number	Percent Absorbed
GMB-02-0	6.49%
GMB-02-1	6.10%
GMB-02-2	5.98%
GMB-02-3	5.93%

Sample Number	Percent Absorbed
GMB-03-0	6.51%
GMB-03-1	6.13%
GMB-03-2	6.05%
GMB-03-3	6.24%

From the results, it is apparent that porosity varies somewhat between samples, even those that have been treated identically and are the product of the same manufacturer. It is notable that in this test, the samples that were washed with the cleaner were less porous than the unwashed samples, albeit at a level of questionable significance. This correlation may be explained as the result of the deposition of colloidal silicofluorides on the surface of the terracotta, blocking the pores. Regardless of the explanation, it is certain that the cleaning process had some effect on the physical properties of the terracotta samples.

Quantification of Change

As discussed in Chapter Four, several methods for quantifying the physical

changes caused by the cleaning process were investigated. The results are summarized below.

SCANNING ELECTRON MICROSCOPY AND ZIDAS MEASUREMENT

The scanning electron micrographs measured using the Zidas machine are seen in Appendix B. The ratio of pores to solid surface over a given area is outlined in the following chart. It is notable that in selecting areas to be photographed under the microscope, it was much easier to find an area containing pores on the multiple-washed samples than on the unwashed and once-washed samples. While we have yet to discover a method to quantify overall change and opening of new pores, this qualitative observation confirms the conclusions of previous research.[88]

SAMPLE NUMBER	PERCENTAGE OF THE SURFACE AREA OCCUPIED BY PORES	AVERAGE PERCENTAGE SURFACE AREA OCCUPIED BY PORES
BV-01-0A	0.217%	0.76%
BV-01-0B	0.742%	
BV-01-0C	1.315%	
BV-01-3A	0.427%	0.43%
BV-01-3B	0.412%	
BV-01-3C	0.447%	
GMB-01-0A	0.700%	1.27%
GMB-01-0B	1.151%	
GMB-01-0C	1.944%	

[88] Matero et. al. observed an increase in the size of and connection between surface pores in their study of the Brooklyn Historical Society. The observations of this thesis imply that more of the total surface area is encompassed by pores.

GMB-01-3A	2.536%	2.46%
GMB-01-3B	2.169%	
GMB-01-3C	1.919%	
GMB-01-3D	3.232%	

Although qualitative assessment implies that a greater percentage of the surface is encompassed by pore space, this is not borne out in the quantitative assessment. The results of this assessment are decidedly inconclusive. The values obtained for surface area varies widely between micrographs of the same sample. While an average pore area was obtained for purposes of comparison, the deviation of the actual values from the average is too large for statistical accuracy.

This method is flawed for many reasons. Aside from the flaws inherent in using SEM for quantitative analysis discussed in Chapter Four, this specific method introduces several possibilities for human error and subjectivity. First, the operative chooses areas of the sample to photograph, and may choose a representative area or an area that is rich in pores. As long as the criteria guiding this choice are clearly stated, this is not a significant problem; however, a problem arises from choosing similar areas from each sample. The operative may attempt to find a pore or series of pores of approximately the same size in each sample, but samples similar in appearance may have very different pore size distributions. This is witnessed by the results seen above, where the author made a concerted effort to find areas with similar sized pores and pore clusters, but the pore size distribution varies widely within each sample.

The Zidas introduces potential for human error in two important ways. First,

the operative must decide what constitutes a pore, what is surface irregularity, and what is simply shadow. These are questions that are easily answered by adjusting the magnification and focus when using the scanning electron microscope, but are less easily answered when limited to a photograph. As long as the operative is consistent in his/her assessment, however, this problem can be minimized. The other problem that arises is in human control of the Zidas sensor. The operative moves the sensor around the perimeter of the pore. Slight variations are inevitable, particularly when tracing the smallest pores. The Zidas does not measure the smallest pores (those with a diameter of less than one micron) easily; often, several attempts are necessary before a valid measurement is obtained. These variations can have a tremendous impact on the overall pore size distribution of the sample.

For this method to be more accurately applied to determining pore size distribution, it is necessary to make a few adjustments. Several micrographs should be evaluated for each sample to create a more valid pore size distribution. By increasing the total surface area evaluated, the pore size distributions would more accurately reflect the variations in the surface of the sample. Additionally, a higher magnification would allow for more accurate measurements of small pores. Even with these improvements, however, the human error introduced by the Zidas will remain unchanged.

Human Touch Assessment

The results of the human touch assessment were somewhat disappointing. In the pre-test, the participants consistently ranked the tiles in the same order, with GMB-

03-0 as the roughest, GMB-03-1 as second, GMB-03-2 as third, and GMB-03-3 as the smoothest. The Boston Valley samples were more difficult for the participants to rank, and the results were less uniform.

The results of the actual test are far less consistent than the results of the pre tests. Often, the participants agreed on the roughest and/or smoothest tiles of a given set, but did not agree on the roughness of the other two. For example, in the BV-03 series, the participants consistently chose BV-03-3 as the roughest tile. However, each of the remaining three tiles was chosen by at least two of the participants as the smoothest.

Sample Number	Average Value
BV-02-0	2.7
BV-02-1	1.6
BV-02-2	3.0
BV-02-3	2.7

Sample Number	Average Value
BV-03-0	2.5
BV-03-1	3.6
BV-03-2	1.6
BV-03-3	3.9

Sample Number	Average Value
GMB-02-0	3.2
GMB-02-1	2.7
GMB-02-2	2.2
GMB-02-3	1.9

Sample Number	Average Value
GMB-03-0	3.8
GMB-03-1	3.1
GMB-03-2	1.8
GMB-03-3	1.3

In order to translate the results into a quantifiable commodity, each assessment was assigned a value. If the participants rated a tile as the roughest of the four, it was assigned a value of four. If it was rated simply "rough," it was assigned a

value of 3. If it was rated "smooth," it was assigned a value of 2, and if it was rated as the "smoothest," it was assigned a value of one. The numerical assessments for each tile were then averaged, and the results compared.

For the Boston Valley samples, there was not a quantifiable link between the number of times the sample was washed and its roughness as determined by the participants. Every participant individually complained of the difficulty of differentiating between the samples in each Boston Valley sample set. However, the relationship between the number of times the sample was washed and the smoothness was much clearer for the Gladding McBean samples; the more times a sample was washed, the smoother it felt to the participants.

It is notable that the participants' opinions varied widely, and produced very inconsistent results. The averages tabulated are in some ways misleading, as they may represent a consistent assessment of "smooth" or "rough," or may be the result of half of the participants rating the tile as roughest, and half of the participants rating the sample as smoothest. Full data from this experiment is available in Appendix B.

Water Drop Absorption

Sample Number	Water absorption %
BV-02-0	100.00%
BV-02-1	70.09%
BV-02-2	41.62%
BV-02-3	43.79%

Sample Number	Water absorption %
BV-03-0	100.00%
BV-03-1	103.55%
BV-03-2	79.70%
BV-03-3	76.00%

SAMPLE NUMBER	WATER ABSORPTION %
GMB-02-0	100.00%
GMB-02-1	56.89%
GMB-02-2	74.74%
GMB-02-3	78.21%

SAMPLE NUMBER	WATER ABSORPTION %
GMB-03-0	100.00%
GMB-03-1	65.35%
GMB-03-2	65.51%
GMB-03-3	32.82%

The unwashed sample was used as a reference; accordingly, the water absorption percentage of the treated samples is the relative amount of water absorbed by that sample in the amount of time that 100% of the water had been absorbed into the reference sample.

The water drop absorption test results are inconclusive. Although the washed samples generally absorbed water at a slower rate than the unwashed samples, there is no recognizable pattern visible among the washed samples.

WATER VAPOR TRANSMISSION

SAMPLE NUMBER	WATER ABSORPTION %
BV-13-0	2.35×10^{-9}
BV-13-3	3.68×10^{-9}
BV-14-0	2.41×10^{-9}
BV-14-3	2.25×10^{-9}
BV-15-0	3.46×10^{-9}
BV-15-3	2.30×10^{-9}

SAMPLE NUMBER	WATER ABSORPTION %
GMB-13-0	1.83×10^{-9}
GMB-13-3	1.04×10^{-9}
GMB-14-0	2.38×10^{-9}
GMB-14-3	1.73×10^{-9}
GMB-15-0	3.22×10^{-9}
GMB-15-3	2.02×10^{-9}

The results of the water vapor transmission test do indicate trends, but repeat tests are necessary to provide more complete and representative data. Two of the three sets of Gladding McBean samples were eliminated from the test due to contamination, as the specimen accidentally came into contact with the water in the test container. In the remaining set of samples, the unwashed sample was more permeable than the thrice washed samples. A similar trend is visible for the Boston Valley samples; in two of the three sets of samples, the unwashed tile is more permeable than the washed tile, although the third deviates significantly. This reflects the trend of decreasing porosity after treatment with the cleaning solution.

Simulated Weathering Tests

Full results of each of the simulated weathering tests are found in Appendix A.

Salt Crystallization

The salt crystallization test revealed an interesting pattern that shows an indisputable correlation with the frequency of treatment.

Sample Number	Weight Gain
BV-04-0	1.95%
BV-04-1	6.19%
BV-04-2	6.87%
BV-04-3	6.49%

Sample Number	Weight Gain
BV-05-0	1.45%
BV-05-1	6.27%
BV-05-2	6.35%
BV-05-3	6.35%

Sample Number	Weight Gain
BV-06-0	1.35%
BV-06-1	5.51%
BV-06-2	6.31%
BV-06-3	6.07%

Sample Number	Weight Gain
GMB-04-0	0.03%
GMB-04-1	0.61%
GMB-04-2	0.92%
GMB-04-3	0.96%

Sample Number	Weight Gain
GMB-05-0	1.77%
GMB-05-1	0.66%
GMB-05-2	5.69%
GMB-05-3	7.88%

Sample Number	Weight Gain
GMB-06-0	0.46%
GMB-06-1	1.35%
GMB-06-2	1.99%
GMB-06-3	5.52%

There is a dramatic increase in percent weight gain between unwashed and once washed samples, indicating a significant increase in susceptibility of the samples to damage due to salt crystallization. Although this test did not cause damage to the samples as measured in weight loss, it is possible that the amount of salts present are proportional to potential damage. To determine whether there is a definitive correlation between weight gain and ultimate damage, this test should be repeated and continued until the samples lose significant amounts of weight.

An interesting trend is visible in the sets of samples. In two of the sets of Boston Valley samples, the tile that had the greatest percentage weight gain was the twice washed tile.[89] This could be explained by the reduction in porosity in the multiple washed tiles; colloidal silica may have been blocking some of the pores of the thrice washed samples, preventing the salt solution from penetrating the pores and the salts from crystallizing within. However, this theory is not compatible with the results of the Gladding McBean samples. These thrice washed sample gained the most weight in each set of samples.

Accelerated Weathering

The samples exposed to the accelerated weathering chamber revealed patterns of weight loss that appear to have a correlation with the frequency of exposure to the cleaning solution.

Sample Number	Weight Loss
BV-10-0	0.02%
BV-10-1	0.10%
BV-10-2	0.60%
BV-10-3	0.21%

Sample Number	Weight Loss
BV-11-0	0.34%
BV-11-1	0.01%
BV-11-2	0.01%
BV-11-3	0.20%

Sample Number	Weight Loss
BV-12-0	0.02%
BV-12-1	0.05%
BV-12-2	0.51%
BV-12-3	0.18%

Sample Number	Weight Loss
GMB-10-0	0.04%
GMB-10-1	0.02%
GMB-10-2	1.11%
GMB-10-3	0.66%

Sample Number	Weight Loss
GMB-11-0	0.05%
GMB-11-1	0.41%
GMB-11-2	1.06%
GMB-11-3	0.65%

Sample Number	Weight Loss
GMB-12-0	0.06%
GMB-12-1	0.46%
GMB-12-2	1.17%
GMB-12-3	0.72%

Analysis of the patterns of weight change for samples exposed to the accelerated weathering machine exhibit a pattern similar to that seen in salt crystallization. With one exception, the sample of each set that had the most significant weight loss was the twice washed sample. However, for all of the samples, the percentage of weight lost was relatively small, probably due to the somewhat moderate conditions of exposure within the chamber. If the samples had been exposed to the more severe temperatures recommended by the ASTM standard, it is likely that

[89] In the third set of samples, the twice and thrice washed samples had equal weight gain percentages.

more significant weight loss would have occurred. Prolongation of the testing cycle and increased severity of conditions are required to verify potential trends.

Freeze/Thaw

The samples exposed to fifty freeze/thaw cycles were relatively unchanged by the procedure.

Sample Number	Weight Loss
BV-07-0	0.011%
BV-07-1	0.044%
BV-07-2	0.067%
BV-07-3	0.048%

Sample Number	Weight Loss
BV-08-0	0.029%
BV-08-1	0.033%
BV-08-2	0.030%
BV-08-3	0.041%

Sample Number	Weight Loss
BV-09-0	0.018%
BV-09-1	0.037%
BV-09-2	0.042%
BV-09-3	0.056%

Sample Number	Weight Loss
GMB-07-0	0.025%
GMB-07-1	0.025%
GMB-07-2	-1.088%
GMB-07-3	0.041%

Sample Number	Weight Loss
GMB-08-0	0.041%
GMB-08-1	0.042%
GMB-08-2	-0.491%
GMB-08-3	0.038%

Sample Number	Weight Loss
GMB-09-0	0.049%
GMB-09-1	0.016%
GMB-09-2	0.008%
GMB-09-3	0.060%

A pattern of weight loss is recognizable for the Boston Valley samples. For two of the three sample sets, the amount of weight lost increased with repeated exposures to the cleaning solution. For the third sample set, the sample that was washed twice had greater loss than the sample that was washed once. A similar pattern does not exist for the Gladding McBean samples. The results of this test are much less consistent, with the highest percentage of weight loss within a sample set

occurring in both the unwashed and thrice washed samples.

Although the Boston Valley samples do exhibit recognizable patterns of weight loss, this weight loss is not significant. According to the ASTM standard, a weight loss of 0.5% or greater results in failure of the test. As none of the samples exhibited weight loss approaching this limit, it is impossible to draw conclusions from this test.

The results of this test may be slightly skewed due to a testing problem. Two of the samples actually gained weight, seemingly an impossibility. However, as instructed by the standard, the samples were kept in metal containers, which rusted during the process. While a significant effort was made to keep the thawing chamber free of rust particles, and the samples were thoroughly rinsed and blotted to remove any excess rust debris before drying them to a constant weight, it seems likely that rust particles are the cause of the weight gain.

CHAPTER SIX: CONCLUSIONS

Previous research has demonstrated that hydrofluoric acid based cleaners alter the pore structure of the fireskin surface of unglazed architectural terracotta. The stated goals of this thesis are to describe and quantify these changes and assess the impact that the changes have on long term performance of the material.

Quantification of the changes to the porosimetry of the fireskin proved challenging. Several methods were employed, each with distinct advantages and flaws. The most unique method was the measurement of pores seen in scanning electron micrographs using the Zidas machine. Although this technique is innovative, the inherent flaws of the method require assumptions that go beyond the limit of scientific acceptability. Additionally, the opportunities for human subjectivity and error defeat the objective nature of quantification, thereby rendering the technique ineffective.

The human touch assessment was also problematic, as human touch was generally subjective and not sensitive enough to detect the changes to the surface caused by the cleaner. While the water absorption rate indicated that in general the samples had become less porous as a result of exposure to the cleaner, the numerical differences were not consistent enough to allow for quantification based on this technique.

The type of quantification technique required for a given situation is dependent on the purpose it is intended to serve. If quantification is intended to prove absolutely that changes occur to the porosimetry of the surface of the sample, then it would be

wise to continue to investigate more sensitive analytical techniques, such as laser triangulation profilometry. However, if it is not necessary to numerically prove a change to the size of the pores, the effects of the treatment can be assessed quantitatively through simpler laboratory methods such as water absorption.

The second goal of this thesis was to assess the impact of hydrofluoric acid based cleaners on the weathering behavior of terracotta. The results of the simulated weathering tests were interesting and contradictory. The salt crystallization test indicates that the most noticeable and significant change to the porosity of the terracotta comes after a single exposure to the cleaner. An average of more than twice as much salt was absorbed by the once washed samples than the unwashed samples. The dramatic change between the unwashed and once washed samples indicates change to the pore structure of the samples and predicts resulting damage. It is notable that if a sample is treated with the solution, a third treatment appears to improve its resistance to the infiltration of salts.

These assertions are not necessarily confirmed by the results of the other simulated weathering tests, however. The samples exposed to the accelerated weathering chamber showed patterns of increased loss for the washed samples, but not necessarily at a significant level. With one exception, the difference in loss varied from a few hundredths of a percent for unwashed samples to a full percent for twice washed samples. While samples washed three times showed less weight loss than the twice washed samples, all weight loss was relatively small. It would be necessary to perform these tests under more severe conditions in order to draw more definitive

conclusions.

The results of the freeze/thaw tests do not actively support the assertion that the samples become more porous after treatment with the cleaning solution, either. While the washed samples did lose more weight than the unwashed samples, the difference was not significant. In order to draw sound, definitive conclusions, this test would need to be run under more severe conditions for a longer duration.

The question of when *physical alteration* becomes *damage* arises. In the case of the salt crystallization, it is evident that if exposed to a significant source of salts, the surfaces that were treated with a hydrofluoric acid based cleaner might be more prone to decay.

Similarly, the results of the weathering chamber indicate a marked difference between the loss of mass of the unwashed and twice washed samples. Although the ASTM standard for accelerated weathering does not give a definition of failure based on loss of mass, the freeze/thaw test defines weight loss of 0.5% as unacceptable. If this same definition is applied to the samples exposed to the accelerated weathering chamber, four of the twice washed and four of the thrice washed samples would have unacceptable weight loss.

The results of the freeze/thaw test do not indicate that significant damage occurred as a result of the cleaning process. While the samples did lose weight, it was not significant enough to establish a recognizable pattern of deterioration.

It should also be noted that the changes and potential damage observed in these tests may be more pronounced in real field situations involving terra cotta for two

primary reasons. First, this study applied the cleaner according to the manufacturer's instructions, diluted the cleaner as recommended and carefully monitored dwell times. This level of precision and care is not guaranteed in the field, and the lack thereof has been frequently discussed in conservation literature. Increased concentrations and longer dwell times would likely result in greater damage. Second, the terra cotta samples used for the trials are modern, manufactured only weeks before the commencement of testing, and have not been exposed to weathering forces. Modern terracotta is well fired, and accordingly is believed to be more resistant to physical and chemical abrasion than historic terracotta. Moreover, as the samples have not been exposed to the natural environment, they have not experienced the weathering that a building being considered for cleaning has experienced. These factors would improve the samples' resistance to the cleaner, and less change (and damage) would be expected.

This thesis has indicated the need for future study both to improve assessment procedures and to verify and better quantify observed trends. Recommendations for future testing are as follows:

- Further research into quantification techniques is necessary, and laser triangulation profilometry should be explored.
- The conditions of the accelerated weathering chamber should be adjusted to reflect the suggestions of the standard. This will most likely result in more significant loss of mass.
- Sample preparation and conditions for the water vapor transmission test

should be improved. If at all possible, samples should be trimmed into disks and standard water vapor transmission equipment should be employed. The smaller sample size will allow for easier manipulation of the samples during the weighing procedure. Additionally, the environment of the chamber should be conditioned with a salt solution in order to maintain a relative humidity closer to the 50% RH indicated by the standard.

- The water drop absorption test should be performed on a larger number of samples, and the water should be applied with a more precise instrument than a burette. This may improve the accuracy and reproducibility of the results.
- The water vapor transmission and permeability tests should be conducted on more than three sets of tiles to create a larger statistical pool of results. Risk of the operative error resulting in disqualification of a set of samples is significant; by increasing the number of sets of samples, an adequate statistical set of samples will be maintained, and the resulting conclusions will be more valid.
- With these improvements to the testing program, the tests should be repeated with historic terracotta. If possible, it would be preferable to test both unsoiled and soiled historic terracotta which would allow for analysis of the interaction between the cleaner and the historic substrate and evaluation of the role of the soiling in the reaction between the terracotta

and the cleaner. Additionally, the efficacy of the cleaning procedure could be assessed.

- A similar study should be undertaken in the field. Sections of a test wall should be subjected to the same cleaning protocol and monitored for changes over time.
- Further characterization studies are needed to assess the differences between samples that have been washed twice and three times. Although the apparent reduction in porosity after the third wash may in fact be the result of the deposition of fluosilicates or other re-precipitated substances, these surface deposits were not visible on the scanning electron micrographs. This discrepancy needs to be addressed. These behavioral changes may be due to changes in porosimetry as a result of exposure to hydrofluoric acid based cleaner. Further investigation into changes in porosimetry should involve use of mercury intrusion porosimetry.

The results of this research indicate that the use of hydrofluoric acid based cleaner causes changes to the structure of the terra cotta surface which affects weathering behavior. Further study is required to better assess the correlation between surface alteration and potential negative effects on durability so as to permit more informed evaluation of the use of hydrofluoric acid based cleaners on unglazed architectural terra cotta.

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Appendix A

Salt Crystallization After 21 Cycles				
Sample Number	First Weight	Pre-Testing Weight	Post-Testing Weight	Percent Weight Gain
BV-04-0	173.84g	173.84g	177.23g	1.95%
BV-04-1	174.64g	174.64g	185.45g	6.19%
BV-04-2	173.60g	173.60g	185.52g	6.87%
BV-04-3	174.13g	174.13g	185.43g	6.49%
BV-05-0	168.39g	168.39g	170.83g	1.45%
BV-05-1	169.92g	169.92g	180.58g	6.27%
BV-05-2	171.84g	171.84g	182.76g	6.35%
BV-05-3	164.05g	164.05g	174.47g	6.35%
BV-06-0	174.58g	174.58g	176.94g	1.35%
BV-06-1	171.90g	171.90g	181.38g	5.51%
BV-06-2	173.03g	173.03g	183.95g	6.31%
BV-06-3	178.35g	178.35g	189.18g	6.07%
GMB-04-0	129.23g	129.23g	129.27g	0.03%
GMB-04-1	113.62g	113.62g	114.31g	0.61%
GMB-04-2	124.50g	124.50g	125.64g	0.92%
GMB-04-3	129.53g	129.53g	130.77g	0.96%
GMB-05-0	118.02g	118.02g	120.11g	1.77%
GMB-05-1	117.84g	117.84g	118.62g	0.66%
GMB-05-2	118.34g	118.34g	125.07g	5.69%
GMB-05-3	121.22g	121.22g	130.77g	7.88%
GMB-06-0	119.14g	119.14g	119.69g	0.46%
GMB-06-1	117.48g	117.48g	119.07g	1.35%
GMB-06-2	117.38g	117.38g	119.71g	1.99%
GMB-06-3	120.60g	120.60g	127.26g	5.52%

ACCELERATED WEATHERING				
SAMPLE NUMBER	FIRST WEIGHT	PRE-TESTING WEIGHT	POST-TESTING WEIGHT	PERCENT WEIGHT LOSS
BV-10-0	169.18g	169.17g	169.13g	0.02%
BV-10-1	171.85g	171.81g	171.63g	0.10%
BV-10-2	183.49g	183.43g	182.33g	0.60%
BV-10-3	170.96g	170.93g	170.57g	0.21%
BV-11-0	176.88g	176.68g	176.08g	0.34%
BV-11-1	177.14g	177.05g	177.13g	0.01%
BV-11-2	164.02g	164.02g	164.00g	0.01%
BV-11-3	170.27g	170.27g	170.24g	0.02%
BV-12-0	155.69g	155.68g	155.65g	0.02%
BV-12-1	168.36g	168.35g	168.27g	0.05%
BV-12-2	170.92g	170.89g	170.01g	0.51%
BV-12-3	165.00g	164.98g	164.68g	0.18%
GMB-10-0	125.05g	125.05g	125.00g	0.04%
GMB-10-1	121.78g	121.77g	121.74g	0.02%
GMB-10-2	115.84g	115.82g	144.53g	1.11%
GMB-10-3	123.56g	123.55g	122.74g	0.66%
GMB-11-0	123.10g	123.09g	123.03g	0.05%
GMB-11-1	123.01g	123.00g	122.49g	0.41%
GMB-11-2	119.08g	119.07g	177.81g	1.06%
GMB-11-3	117.71g	117.71g	116.95g	0.65%
GMB-12-0	115.29g	115.30g	115.23g	0.06%
GMB-12-1	125.60g	125.65g	125.07g	0.46%
GMB-12-2	121.79g	121.78g	120.35g	1.17%
GMB-12-3	121.77g	121.78g	120.90g	0.72%

FREEZE/THAW TEST				
SAMPLE NUMBER	FIRST WEIGHT	PRE-TESTING WEIGHT	POST-TESTING WEIGHT	PERCENT WEIGHT LOSS
BV-07-0	177.15	177.17	177.15g	0.011%
BV-07-1	182.65	182.66	182.58g	0.044%
BV-07-2	163.10	163.11	163.00g	0.067%
BV-07-3	166.28	166.29	166.21g	0.048%
BV-08-0	170.29	170.31	170.26g	0.029%
BV-08-1	184.32	184.34	184.28g	0.033%
BV-08-2	168.20	168.22	168.17g	0.030%
BV-08-3	171.33	171.35	171.28g	0.041%
BV-09-0	165.72	165.73	165.70g	0.018%
BV-09-1	164.08	164.09	164.03g	0.037%
BV-09-2	166.33	166.35	166.28g	0.042%
BV-09-3	159.69	159.70	159.61g	0.056%
GMB-07-0	119.82	119.82	119.79g	0.025%
GMB-07-1	118.30	118.31	118.28g	0.025%
GMB-07-2	133.31	133.33	134.78g	+1.088%
GMB-07-3	122.34	122.35	122.30g	0.041%
GMB-08-0	122.03	122.04	121.99g	0.041%
GMB-08-1	119.80	119.81	119.76g	0.042%
GMB-08-2	124.13	124.15	124.76g	+0.491%
GMB-08-3	130.75	130.77	130.72g	0.038%
GMB-09-0	122.61	122.62	122.56g	0.049%
GMB-09-1	121.27	121.28	121.26g	0.016%
GMB-09-2	119.09	119.10	119.09g	0.008%
GMB-09-3	117.29	117.29	117.22g	0.060%

Appendix A

Crystallization of Salts Pre-Test			
Sample Number	Pre-Testing Weight	Post-Testing Weight	Percent Weight Gain
BV-Salts-0	165.61g	177.03g	6.90%
BV-Salts-3	172.55g	185.28g	7.38%
GMB-Salts-0	122.36g	122.51g	.012%
GMB-Salts-3	123.40g	130.10g	5.43%

Accelerated Weathering Pre-Test			
Sample Number	Pre-Testing Weight	Post-Testing Weight	Percent Weight Gain
BV-Weather-0	159.18g	159.20g	.01%
BV-Weather-3	167.65g	167.67g	.01%
GMB-Weather-0	120.46g	120.48g	.02%
GMB-Weather-3	124.30g	123.60g	.56%

Freeze/Thaw Pre-Test			
Sample Number	Pre-Testing Weight	Post-Testing Weight	Percent Weight Loss
BV-F/T-0	163.60g	163.50g	.06%
BV-F/T-3	155.42g	155.34g	.05%
GMB-F/T-0	120.01g	119.96g	.04%
GMB-F/T-3	123.08g	123.03g	.04%

APPENDIX B

POROSITY			
SAMPLE NUMBER	DRY WEIGHT	SATURATED WEIGHT	% ABSORPTION
BV-02-0	170.87 g	182.78 g	6.97%
BV-02-1	160.39 g	171.00 g	6.62%
BV-02-2	162.59 g	173.50 g	6.71%
BV-02-3	164.78 g	175.64 g	6.59%
BV-03-0	163.29 g	174.40 g	6.80%
BV-03-1	174.95 g	186.41 g	6.55%
BV-03-2	163.16 g	173.84 g	6.55%
BV-03-3	164.47 g	175.32 g	6.60%
GMB-02-0	123.59 g	131.61 g	6.49%
GMB-02-1	127.80 g	135.60 g	6.10%
GMB-02-2	126.85 g	134.44 g	5.98%
GMB-02-3	126.21 g	133.70 g	5.93%
GMB-03-0	117.87 g	125.54 g	6.51%
GMB-03-1	117.84 g	125.06 g	6.13%
GMB-03-2	117.20 g	124.29 g	6.05%
GMB-03-3	118.00 g	125.36 g	6.24%

APPENDIX B

WATER DROP ABSORPTION			
SAMPLE NUMBER	REFERENCE SAMPLE	TREATED SAMPLE	PERCENT WATER ABSORPTION
	TOTAL SECONDS	TOTAL SECONDS	
BV-02-0	839	839	100.00%
BV-02-1	839	1197	70.09%
BV-02-2	839	2016	41.62%
BV-02-3	839	1916	43.79%
BV-03-0	1343	1343	100.00%
BV-03-1	1343	1297	103.55%
BV-03-2	1343	1685	79.70%
BV-03-3	1343	1767	76.00%
GMB-02-0	1012	1012	100.00%
GMB-02-1	1012	1779	56.89%
GMB-02-2	1012	1354	74.74%
GMB-02-3	1012	1294	78.21%
GMB-03-0	1075	1075	100.00%
GMB-03-1	1075	1645	65.35%
GMB-03-2	1075	1641	65.51%
GMB-03-3	1075	3275	32.82%

Appendix B

		Claudia	Catherine	Elizabeth	Kelly	Lori	Elsa	Joshua	Chris	Mary	Andrea
BV-02	Roughest	2	0	0	3	1	0	3	0	3	3
	Rough	1	2	3	2	2	2	2	2	2	2
	Smooth	0	3	2	0	3	1	0	3	0	0
	Smoothest	3	1	1	1	0	3	1	1	1	1
BV-03	Roughest	3	3	3	3	3	0	3	3	3	3
	Rough	1	0	0	0	1	3	1	1	0	0
	Smooth	0	2	2	2	2	1	0	2	1	2
	Smoothest	2	1	1	1	0	2	2	0	2	1
GMB-02	Roughest	0	1	0	0	1	0	1	0	0	3
	Rough	3	2	2	1	3	2	0	2	2	1
	Smooth	1	0	1	3	2	1	2	1	3	0
	Smoothest	2	3	3	2	0	3	3	3	1	2
GMB-03	Roughest	0	0	0	0	0	0	1	0	1	0
	Rough	1	1	1	1	3	1	0	1	0	1
	Smooth	3	2	2	2	1	2	2	2	2	2
	Smoothest	2	3	3	3	2	3	3	3	3	3

APPENDIX B

	BV-02-0	BV-02-1	BV-02-2	BV-02-3	BV-03-0	BV-03-1	BV-03-2	BV-03-3
ROUGHEST	4	1	1	4	1	4	0	9
ROUGH	0	1	8	1	5	4	0	1
SMOOTH	5	1	1	3	2	2	6	0
SMOOTHEST	1	7	0	2	2	4	4	0
AVERAGE	2.7	1.6	3	2.7	2.5	3.6	1.6	3.9

	GMB-02-0	GMB-02-1	GMB-02-2	GMB-02-3	GMB-03-0	GMB-03-1	GMB-03-2	GMB-03-3
ROUGHEST	6	3	0	1	8	2	0	0
ROUGH	1	2	5	2	2	7	0	1
SMOOTH	2	4	2	2	0	1	8	1
SMOOTHEST	1	1	3	5	0	0	2	8
AVERAGE	3.2	2.7	2.2	1.9	3.8	3.1	1.8	1.3

Appendix B

Water Vapor Transmission and Permeability							
		Weight In Grams					
Consecutive Weighings	Hours Elapsed	BV-13-0	BV-13-3	BV-14-0	BV-14-3	BV-15-0	BV-15-3
1	0	824.8G	678.3G	678.6G	884.6G	859.0G	838.8G
2	1	824.7G	678.3G	678.7G	884.7G	859.1G	838.8G
3	27	824.1G	677.5G	678.3G	884.3G	858.4G	838.3G
4	50	823.6G	676.8G	678.0G	883.9G	857.9G	837.8G
5	73	823.1G	676.2G	677.6G	883.5G	857.4G	837.4G
6	99	822.5G	675.5G	677.2G	882.7G	856.7G	836.9G
7	123	821.9G	674.9G	676.9G	882.3G	856.2G	836.4G
8	147	821.3G	674.1G	676.3G	881.8G	855.2G	835.8G
9	169	820.8G	673.3G	675.4G	881.4G	854.3G	835.4G
10	193	820.2G	672.6G	674.8G	880.9G	852.9G	834.9G
	G/T	0.02351	0.02919	0.01899	0.01991	0.02947	0.02027
	A	1.3328	1.056	1.05	1.1772	1.1336	1.1766
	WVT	0.017639	0.027645	0.018081	0.016913	0.025993	0.017225
	S	2813.10	2813.10	2813.10	2813.10	2813.10	2813.10
	R_1	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
	R_2	25.90%	25.90%	25.90%	25.90%	25.90%	25.90%
	Permeance	2.35×10^{-9}	3.68×10^{-9}	2.41×10^{-9}	2.25×10^{-9}	3.46×10^{-9}	2.30×10^{-9}

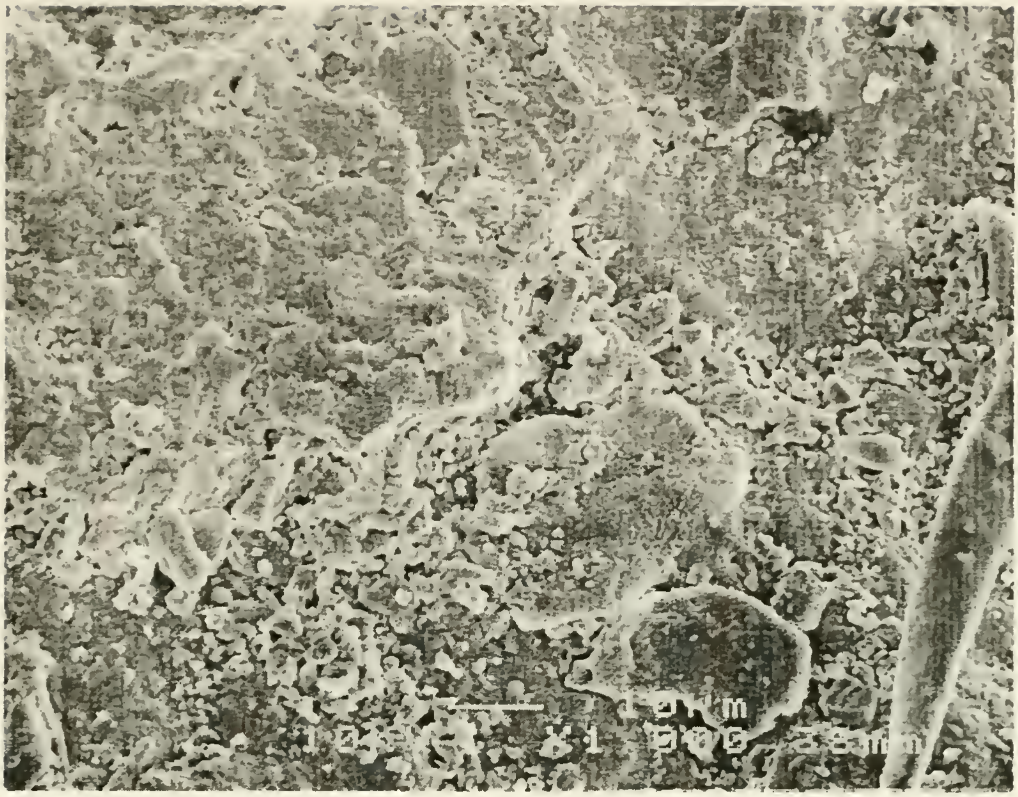
		Weight in Grams					
Consecutive Weighings	Hours Elapsed	GMB-13-0	GMB-13-3	GMB-14-0	GMB-14-3	GMB-15-0	GMB-15-3
1	0	815.7G	786.0G	759.9G	828.1G	773.2G	784.5G
2	1	815.8G	786.0G	759.9G	828.2G	773.2G	784.5G
3	27	815.5G	785.9G	759.5G	827.9G	772.8G	784.2G
4	50	815.2G	785.7G	759.3G	827.6G	772.5G	783.8G
5	73	814.9G	785.5G	758.9G	827.3G	771.8G	783.5G
6	99	814.6G	785.3G	758.6G	827.0G	771.1G	783.1G
7	123	814.3G	785.1G	758.2G	826.7G	770.6G	782.8G
8	147	813.8G	784.9G	757.5G	826.3G	769.8G	782.3G
9	169	813.4G	784.6G	756.8G	825.9G	769.1G	781.9G
10	193	812.9G	784.5G	756.1G	825.5G	768.3G	781.4G
	G/T	0.01431	0.00809	0.01856	0.01350	0.02517	0.01573
	A	1.0404	1.0404	1.0404	1.0404	1.0404	1.0404
	WVT	0.013751	0.007774	0.017844	0.012972	0.024196	0.015121
	S	2813.10	2813.10	2813.10	2813.10	2813.10	2813.10
	R_1	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
	R_2	25.90%	25.90%	25.90%	25.90%	25.90%	25.90%
	Permeance	1.83×10^{-9}	1.04×10^{-9}	2.38×10^{-9}	1.73×10^{-9}	3.22×10^{-9}	2.02×10^{-9}

APPENDIX B

PREFACE TO PORE SIZE DISTRIBUTION CHARTS

The following is the pore size distribution as calculated from the measurements taken on the Zidas machine. For each pore measured, the area, radius, and volume are given in chart form. As explained in Chapter Four, the area of each pore was measured and calculated by the Zidas machine. From this area, the radius and volume of each pore were calculated, assuming that the pores were spherical. While it is apparent from the photographs that the pores are in fact not spherical, it is necessary to make this assumption to determine the pore size distribution. The smaller chart gives a summary of the total surface area and volume occupied by pores in the micrograph examined. The average values for the entire sample (as calculated from the sets of micrographs) are included for the purpose of comparison.

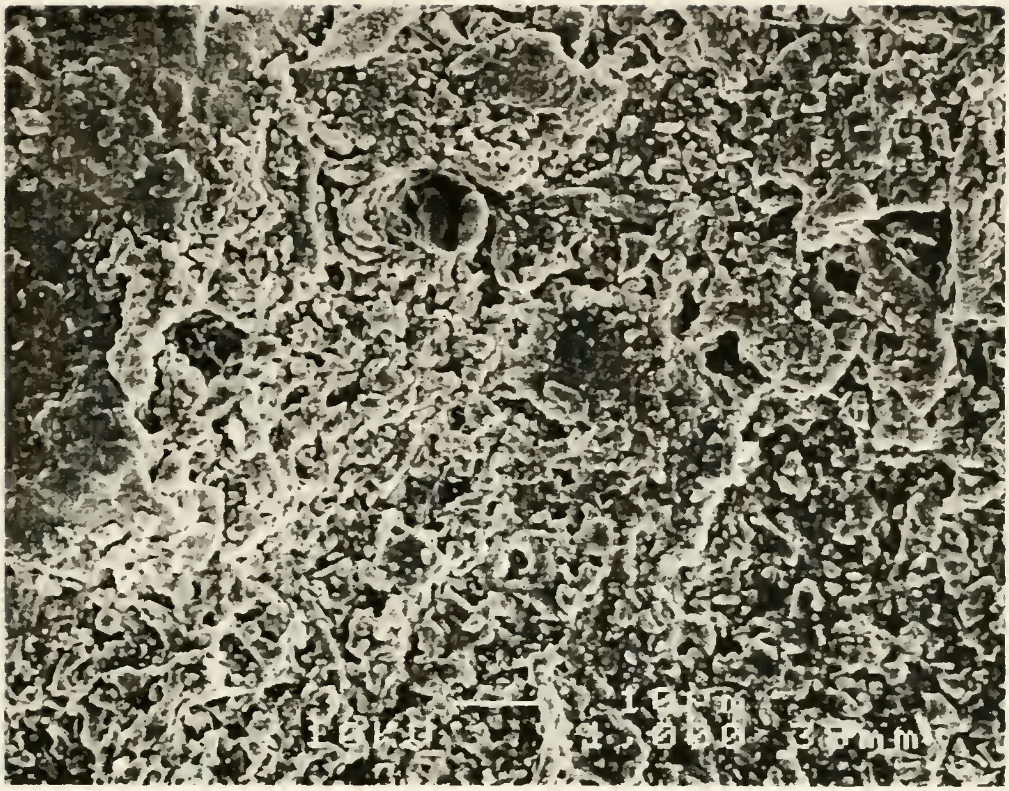
Appendix B
BV-01-0a



BV-01-0a		
Area	Radius	Volume
0.223	0.267	0.079
0.531	0.411	0.291
0.708	0.475	0.448
0.770	0.495	0.508
0.816	0.510	0.554
0.839	0.517	0.578
0.862	0.524	0.602
0.877	0.529	0.618
1.216	0.622	1.009
1.608	0.716	1.534
1.742	0.745	1.730
2.778	0.941	3.484
3.840	1.106	5.662

	BV-01-0a	BV-01-0
Percentage of Surface Area Composed of Pores	0.22%	0.76%
Percentage of Total Volume Composed of Pores	0.04%	0.91%

Appendix B
BV-01-0b



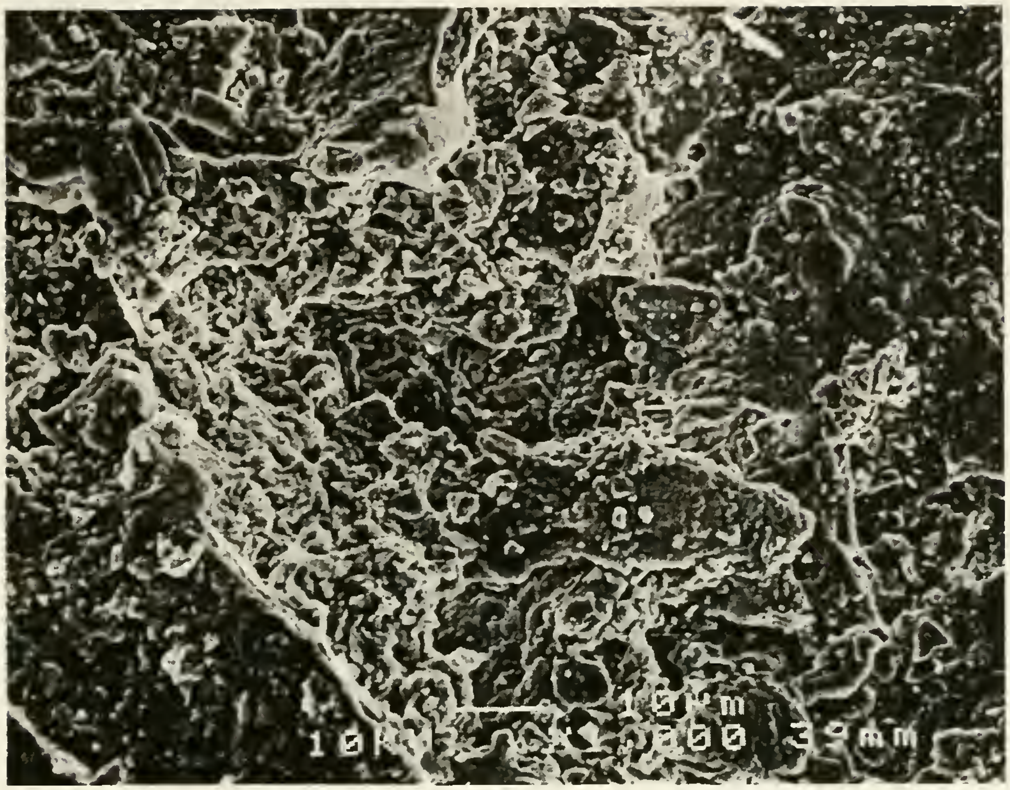
BV-01-0b		
AREA	RADIUS	VOLUME
0.377	0.347	0.174
0.408	0.360	0.196
0.485	0.393	0.254
0.493	0.396	0.260
0.569	0.426	0.323
0.616	0.443	0.363
0.754	0.490	0.493
0.785	0.500	0.523
0.785	0.500	0.523
0.831	0.514	0.570
1.016	0.569	0.771
1.039	0.575	0.797
1.062	0.582	0.823
1.331	0.651	1.155
1.600	0.714	1.523

	BV-01-0b	BV-01-0
Percentage of Surface Area Occupied By Pores	0.74%	0.76%
Percentage of Total Volume Occupied By pores	0.25%	0.91%

APPENDIX B

AREA	RADIUS	VOLUME
1.724	0.741	1.703
1.762	0.749	1.760
1.793	0.756	1.807
1.916	0.781	1.996
2.131	0.824	2.341
2.478	0.888	2.935
2.539	0.899	3.044
6.710	1.462	13.078
9.072	1.700	20.560
15.330	2.210	45.163

APPENDIX B
BV-01-0c



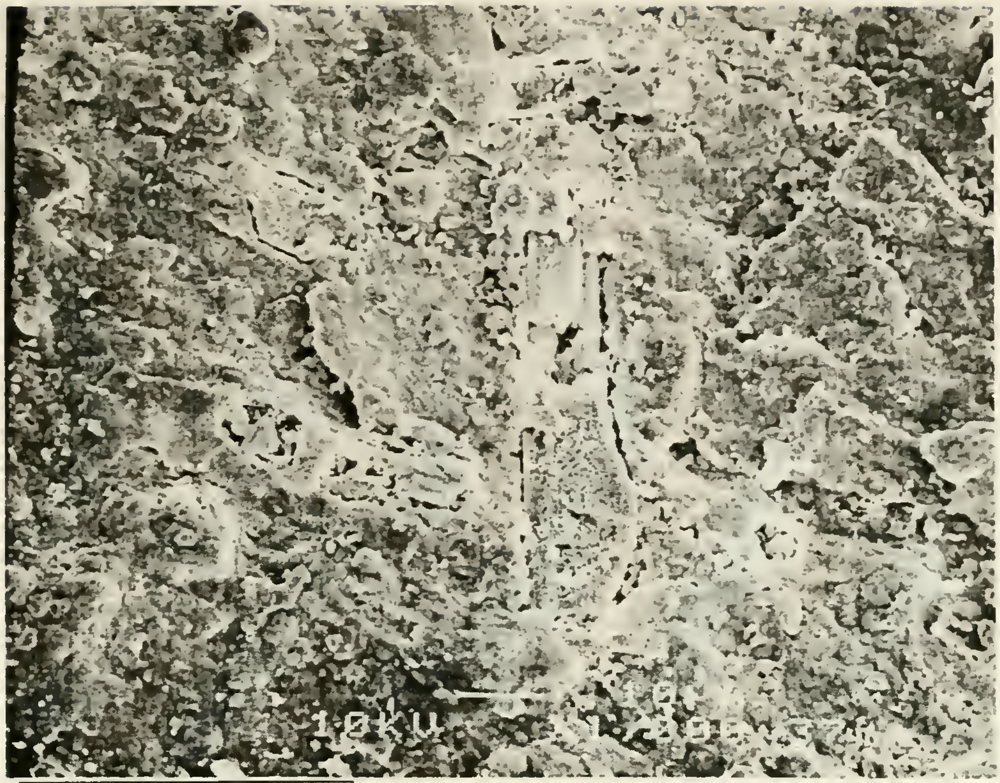
BV-01-0c		
AREA	RADIUS	VOLUME
0.600	0.437	0.350
0.639	0.451	0.384
0.677	0.464	0.419
0.939	0.547	0.684
2.155	0.828	2.380
2.939	0.967	3.791
3.170	1.005	4.247
3.409	1.042	4.736
3.740	1.091	5.442
3.793	1.099	5.558
4.386	1.182	6.912
5.140	1.279	8.768
10.130	1.796	24.260
10.610	1.838	26.004
13.830	2.099	38.700

	BV-01-0c	BV-01-0
PERCENTAGE OF SURFACE AREA COMPOSED OF PORES	1.32%	0.76%
PERCENTAGE OF TOTAL VOLUME COMPOSED OF PORES	0.61%	0.91%

APPENDIX B

AREA	RADIUS	VOLUME
14.580	2.155	41.890
21.360	2.608	74.281

BV-01-3A



BV-01-3A		
AREA	RADIUS	VOLUME
0.239	0.276	0.088
0.308	0.313	0.128
0.346	0.332	0.153
0.362	0.339	0.164
0.500	0.399	0.266
0.500	0.399	0.266
0.531	0.411	0.291
0.554	0.420	0.310
0.600	0.437	0.350
0.600	0.437	0.350
0.754	0.490	0.493
0.770	0.495	0.508
0.785	0.500	0.523
1.139	0.602	0.915
1.477	0.686	1.351
2.262	0.849	2.560

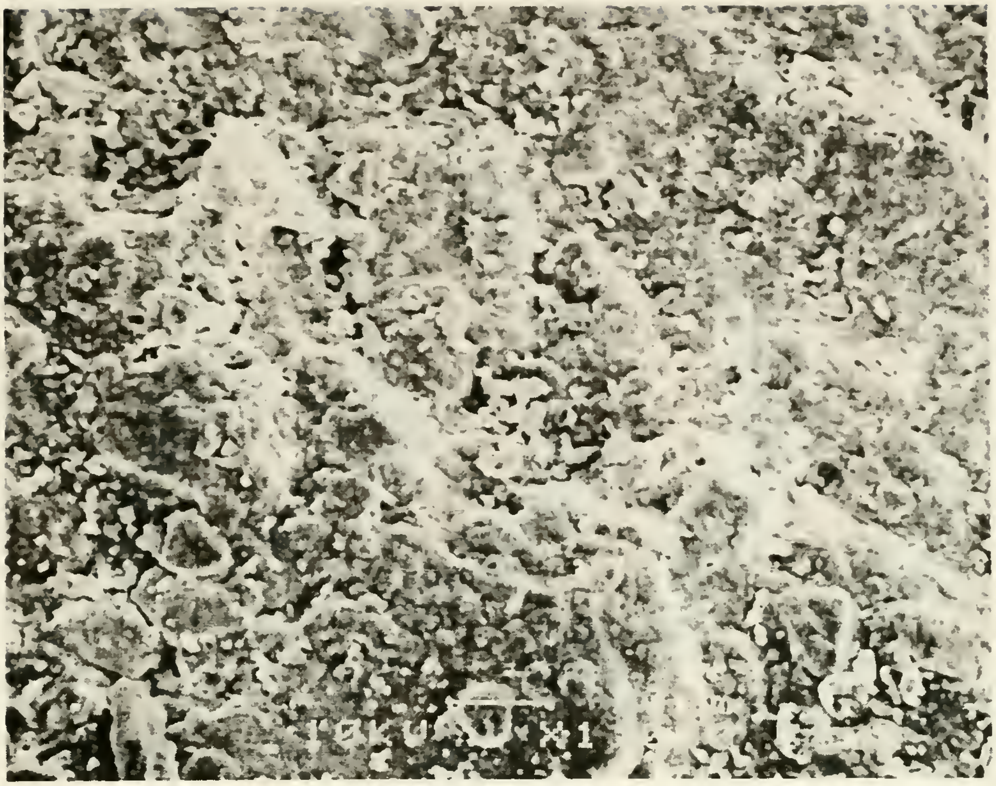
	BV-01-3A	BV-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	0.43%	0.29%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.17%	0.49%

APPENDIX B

AREA	RADIUS	VOLUME
2.778	0.941	3.484
4.501	1.197	7.185
6.017	1.384	11.106
8.133	1.609	17.452

APPENDIX B

BV-01-3B



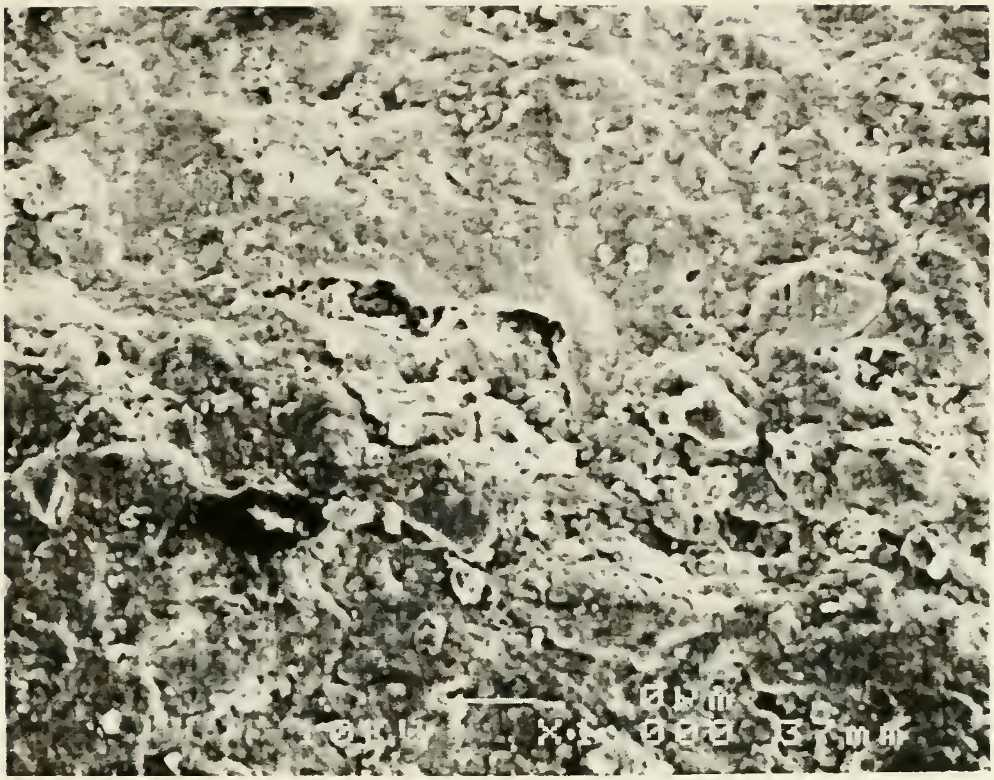
BV-01-3B		
AREA	RADIUS	VOLUME
0.246	0.280	0.092
0.285	0.301	0.114
0.339	0.328	0.148
0.354	0.336	0.158
0.400	0.357	0.190
0.446	0.377	0.224
0.562	0.423	0.317
0.577	0.429	0.330
0.631	0.448	0.377
0.677	0.464	0.419
0.993	0.562	0.744
0.993	0.562	0.744
1.108	0.594	0.878
1.193	0.616	0.980
1.400	0.668	1.246

	BV-01-3B	BV-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	0.41%	0.29%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.17%	0.49%

APPENDIX B

AREA	RADIUS	VOLUME
1.724	0.741	1.703
1.931	0.784	2.019
2.124	0.822	2.329
5.448	1.317	9.568
10.550	1.833	25.784

APPENDIX B
BV-01-3C



BV-01-3C		
AREA	RADIUS	VOLUME
0.292	0.305	0.119
0.362	0.339	0.164
0.385	0.350	0.180
0.469	0.387	0.242
0.531	0.411	0.291
0.569	0.426	0.323
0.708	0.475	0.448
0.752	0.489	0.490
0.916	0.540	0.659
0.993	0.562	0.744
1.000	0.564	0.752
1.131	0.600	0.905
1.277	0.638	1.086
1.839	0.765	1.876
2.078	0.814	2.254

	BV-01-3C	BV-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	0.45%	0.29%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.15%	0.49%

AREA	RADIUS	VOLUME
2.139	0.825	2.354
2.578	0.906	3.115
3.801	1.100	5.576
3.809	1.101	5.594
4.363	1.179	6.857
4.717	1.226	7.709

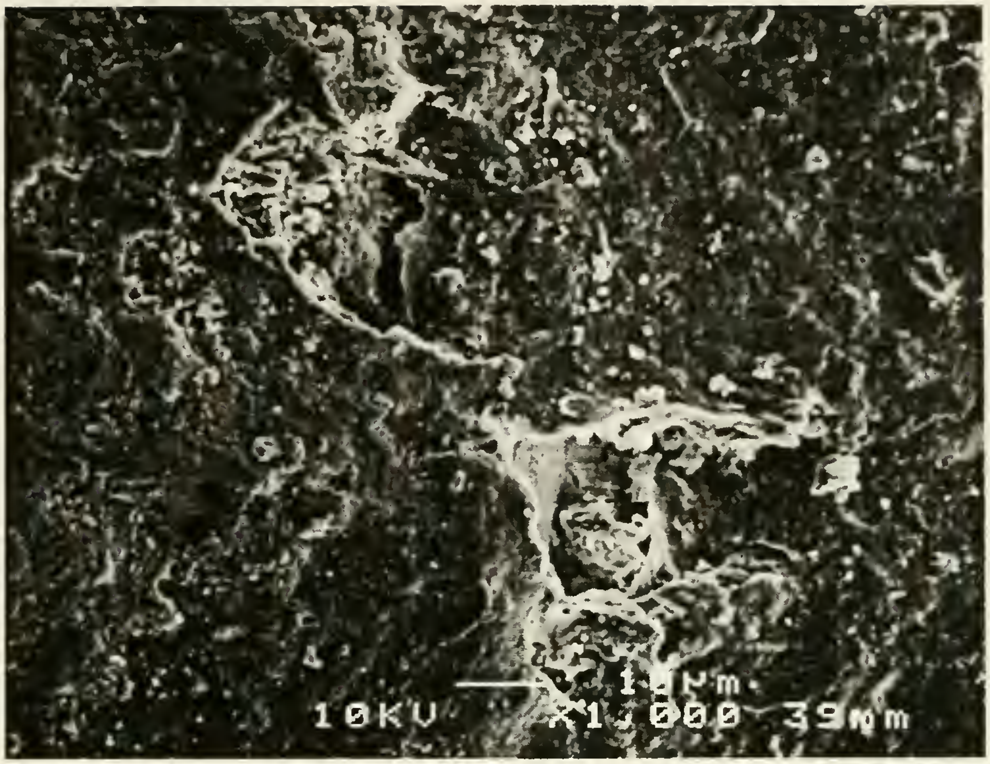
APPENDIX B
GMB-01-0A

GMB-01-0A		
AREA	RADIUS	VOLUME
0.577	0.429	0.330
1.254	0.632	1.057
2.331	0.862	2.678
2.832	0.950	3.586
3.486	1.054	4.897
4.532	1.201	7.260
5.117	1.277	8.710
5.894	1.370	10.767
7.318	1.527	14.896
10.330	1.814	24.982
10.680	1.844	26.262

	GMB-01-0A	GMB-01-0
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	0.70%	1.27%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.15%	0.52%

Appendix B

GMB-01-0B

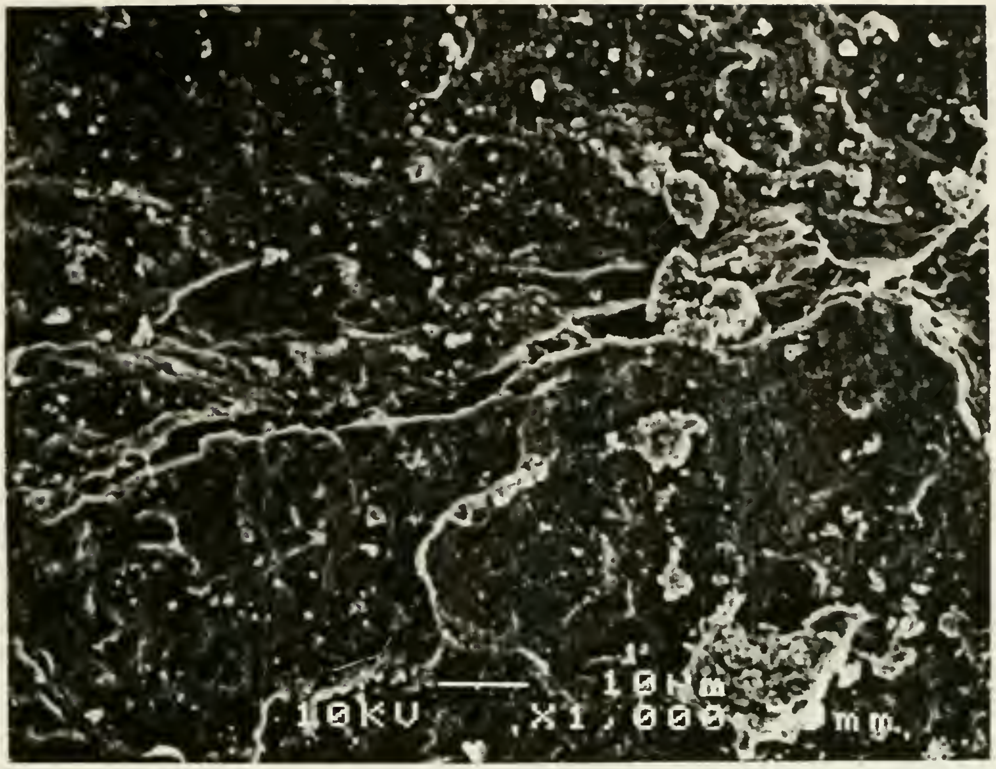


GMB-01-0B		
AREA	RADIUS	VOLUME
0.508	0.402	0.272
0.593	0.434	0.343
0.646	0.454	0.391
0.723	0.480	0.463
0.839	0.517	0.578
0.993	0.562	0.744
1.170	0.610	0.952
1.500	0.691	1.382
1.685	0.733	1.646
2.124	0.822	2.329
2.239	0.844	2.521
2.924	0.965	3.762
3.086	0.991	4.079
3.701	1.086	5.357
7.402	1.535	15.153

	GMB-01-0B	GMB-01-0
Percentage of Surface Area Occupied By Pores	1.15%	1.27%
Percentage of Total Volume Occupied by Pores	0.40%	0.52%

AREA	RADIUS	VOLUME
9.041	1.697	20.455
10.450	1.824	25.418
39.740	3.558	188.502

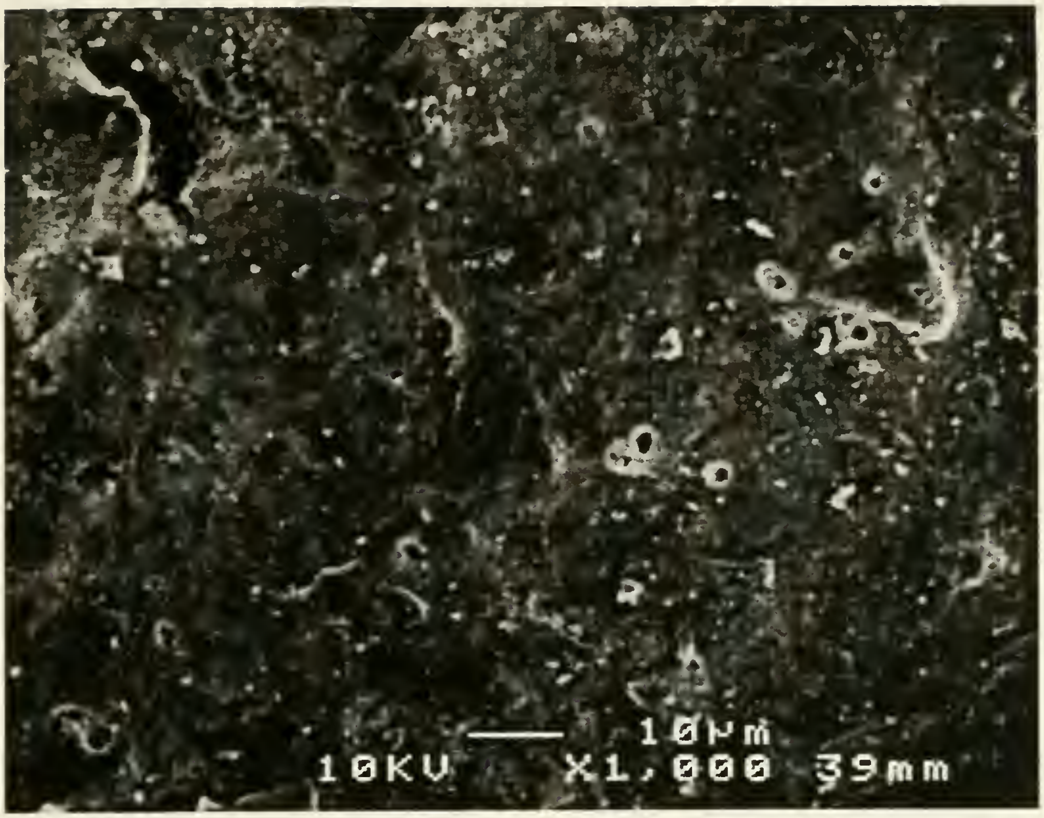
APPENDIX B
GMB-01-0C



GMB-01-0C		
AREA	RADIUS	VOLUME
0.308	0.313	0.128
0.331	0.325	0.143
0.754	0.490	0.493
1.239	0.628	1.038
2.401	0.874	2.799
5.355	1.306	9.324
19.110	2.467	62.859
21.660	2.626	75.851
38.550	3.504	180.099
61.200	4.415	360.248

	GMB-01-0C	GMB-01-0
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	1.94%	1.27%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	1.01%	0.52%

APPENDIX B
GMB-01-3A

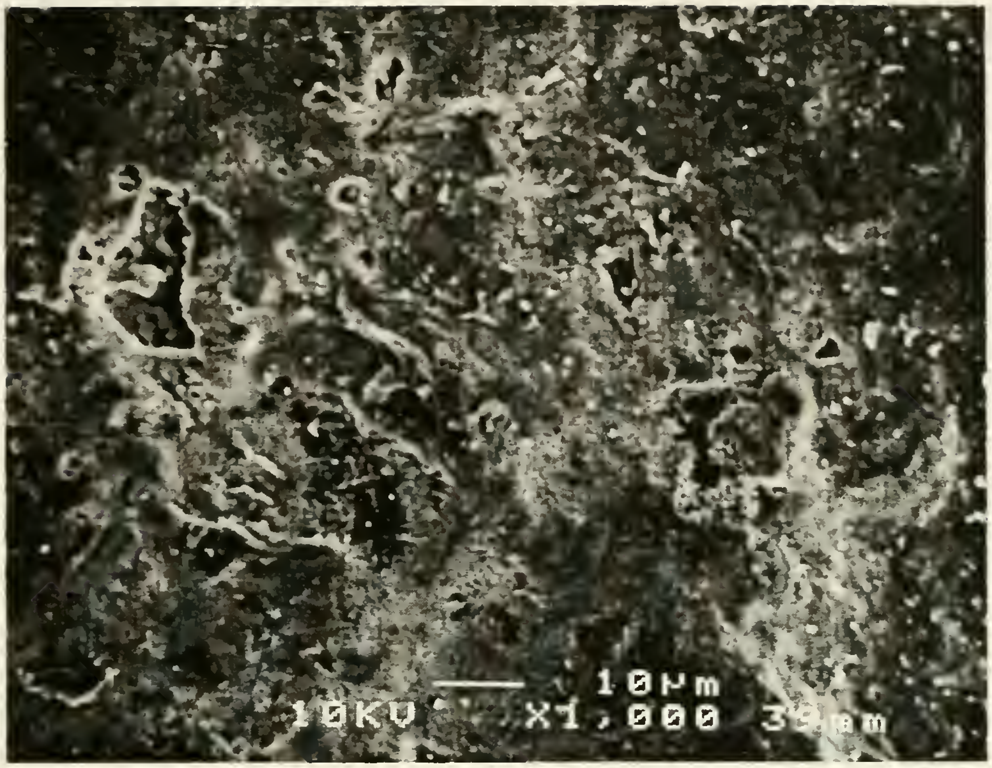


GMB-01-3A		
AREA	RADIUS	VOLUME
0.185	0.243	0.060
0.223	0.267	0.079
0.477	0.390	0.248
0.546	0.417	0.304
0.685	0.467	0.426
0.823	0.512	0.562
0.916	0.540	0.659
1.093	0.590	0.860
1.162	0.608	0.943
1.185	0.614	0.971
1.893	0.776	1.960
1.916	0.781	1.996
2.131	0.824	2.341
2.370	0.869	2.745

	GMB-01-3A	GMB-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	2.54%	2.46%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	1.24%	0.73%

AREA	RADIUS	VOLUME
2.555	0.902	3.073
4.209	1.158	6.497
5.756	1.354	10.391
7.264	1.521	14.731
8.549	1.650	18.808
10.360	1.816	25.091
67.170	4.625	414.226
75.420	4.901	492.837

GMB-01-3B



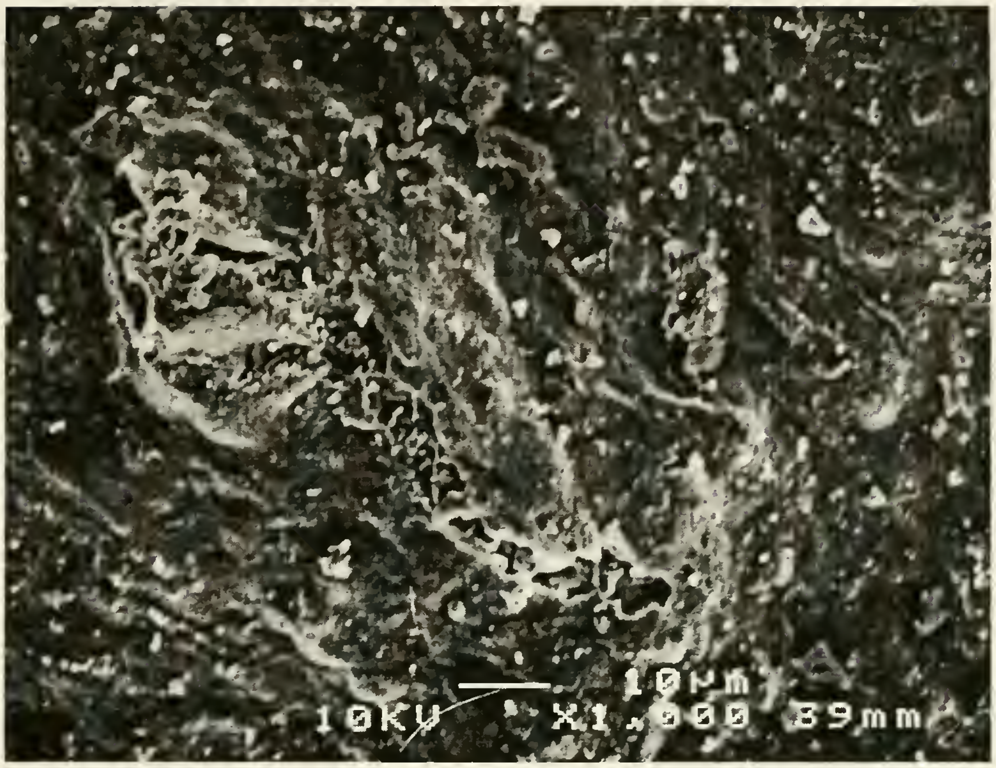
GMB-01-3B		
AREA	RADIUS	VOLUME
0.523	0.408	0.285
1.139	0.602	0.915
1.154	0.606	0.933
1.308	0.645	1.126
1.916	0.781	1.996
2.139	0.825	2.354
2.278	0.852	2.587
2.393	0.873	2.785
3.055	0.986	4.018
3.409	1.042	4.736
3.994	1.128	6.006
4.070	1.138	6.178
4.871	1.246	8.089
5.155	1.281	8.807
11.270	1.895	28.468

	GMB-01-3B	GMB-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	2.17%	2.46%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	1.02%	0.73%

APPENDIX B

AREA	RADIUS	VOLUME
35.260	3.351	157.542
84.410	5.185	583.532

APPENDIX B
GMB-01-3c

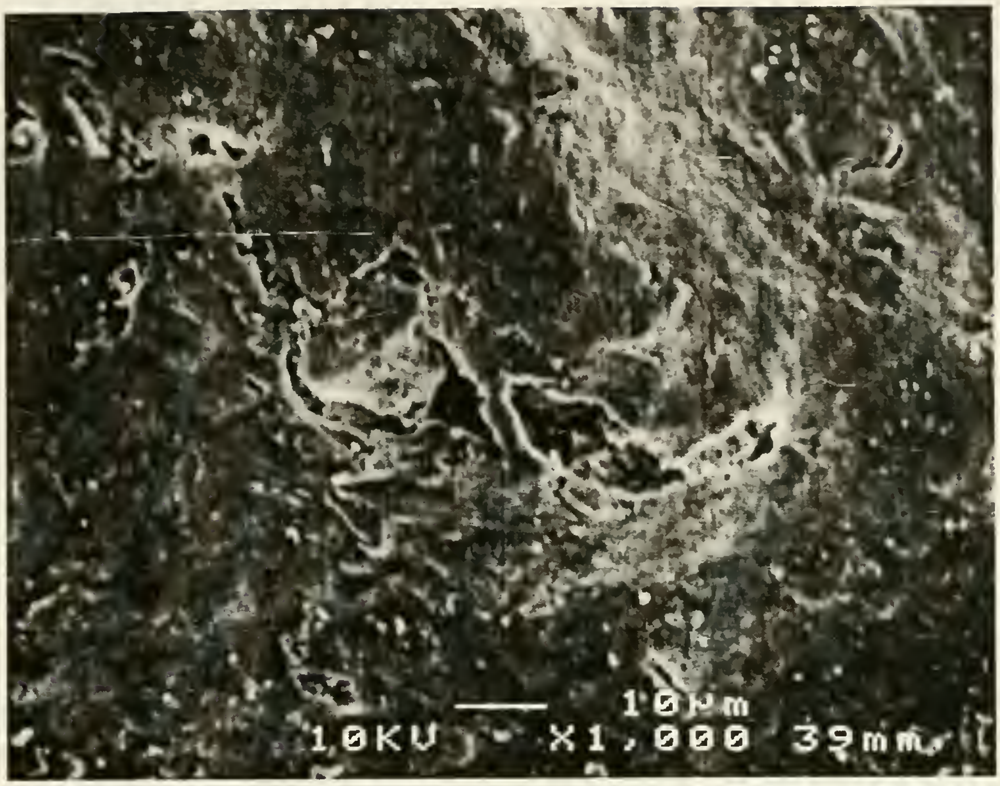


GMB-01-3c		
AREA	RADIUS	VOLUME
0.762	0.493	0.500
0.931	0.545	0.676
0.985	0.560	0.735
1.139	0.602	0.915
1.208	0.620	0.999
1.316	0.647	1.136
1.685	0.733	1.646
3.016	0.980	3.941
4.501	1.197	7.185
4.594	1.210	7.409
5.463	1.319	9.608
5.694	1.347	10.224
7.679	1.564	16.011
8.441	1.640	18.453
28.490	3.012	114.423

	GMB-01-3c	GMB-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	1.92%	2.46%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.66%	0.73%

AREA	RADIUS	VOLUME
29.690	3.075	121.728
43.380	3.717	214.985

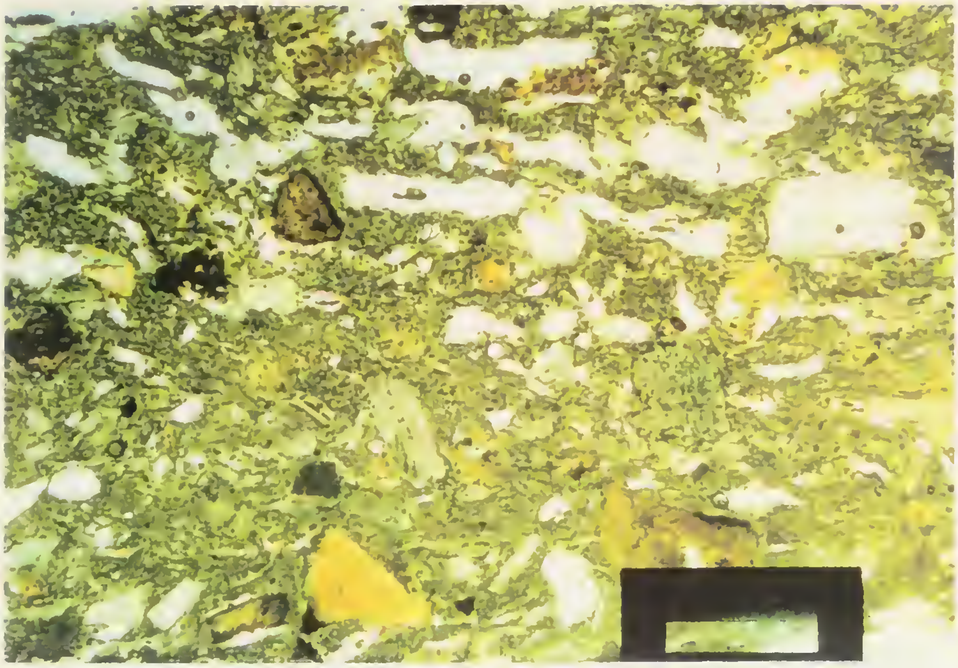
GMB-01-3D



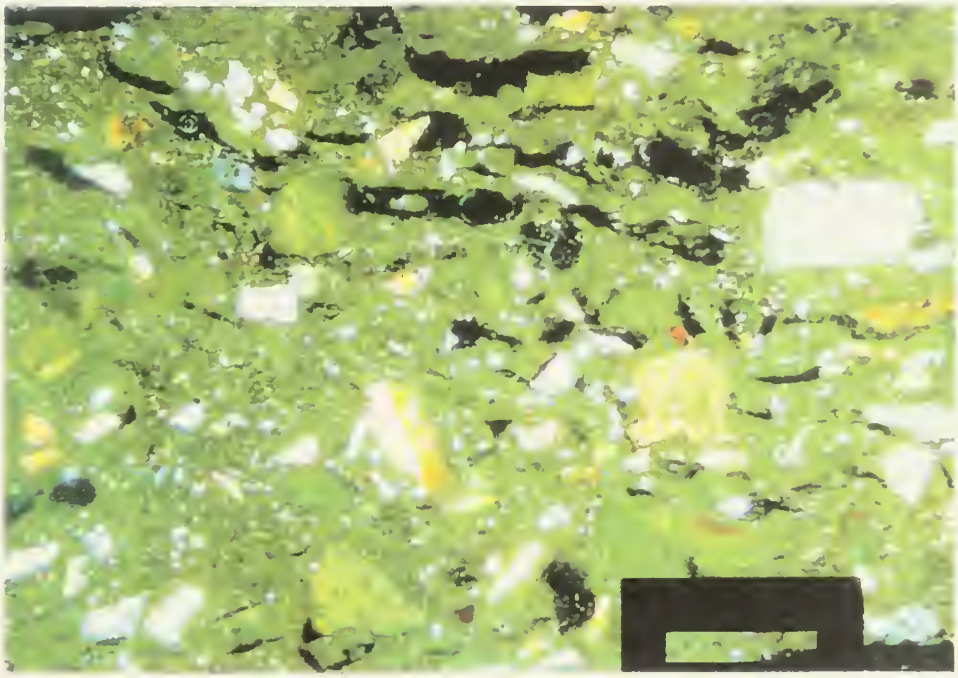
GMB-01-3D		
AREA	RADIUS	VOLUME
0.469	0.387	0.242
0.954	0.551	0.701
1.370	0.661	1.207
1.600	0.714	1.523
1.639	0.722	1.579
2.362	0.867	2.731
3.001	0.978	3.912
3.270	1.020	4.449
3.455	1.049	4.832
3.670	1.081	5.290
6.240	1.410	11.729
11.730	1.933	30.229
12.010	1.956	31.318
12.800	2.019	34.458
13.480	2.072	37.240

	GMB-01-3D	GMB-01-3
PERCENTAGE OF SURFACE AREA OCCUPIED BY PORES	3.23%	2.46%
PERCENTAGE OF TOTAL VOLUME OCCUPIED BY PORES	0.66%	0.73%

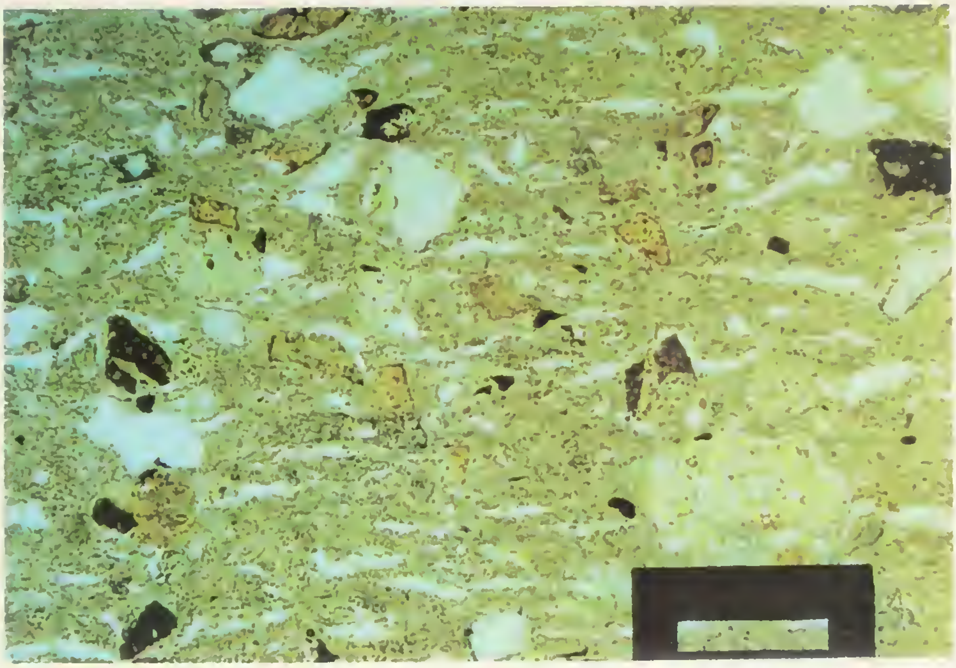
AREA	RADIUS	VOLUME
15.030	2.188	43.844
17.890	2.387	56.936
27.890	2.980	110.827
30.010	3.091	123.701
81.990	5.110	558.618



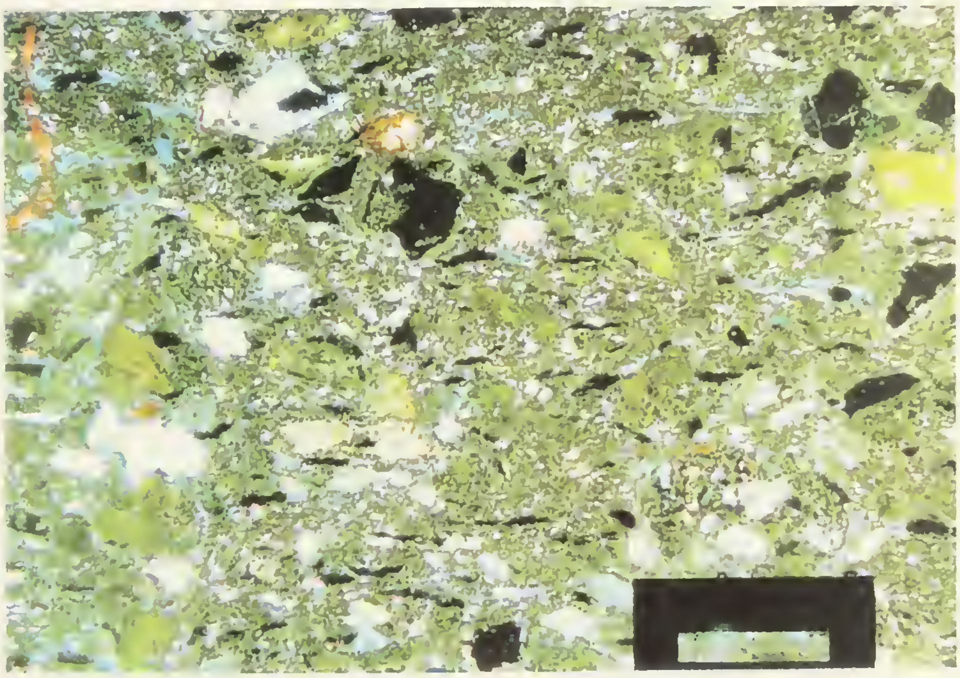
Treated Boston Valley sample at 25X, transmitted light



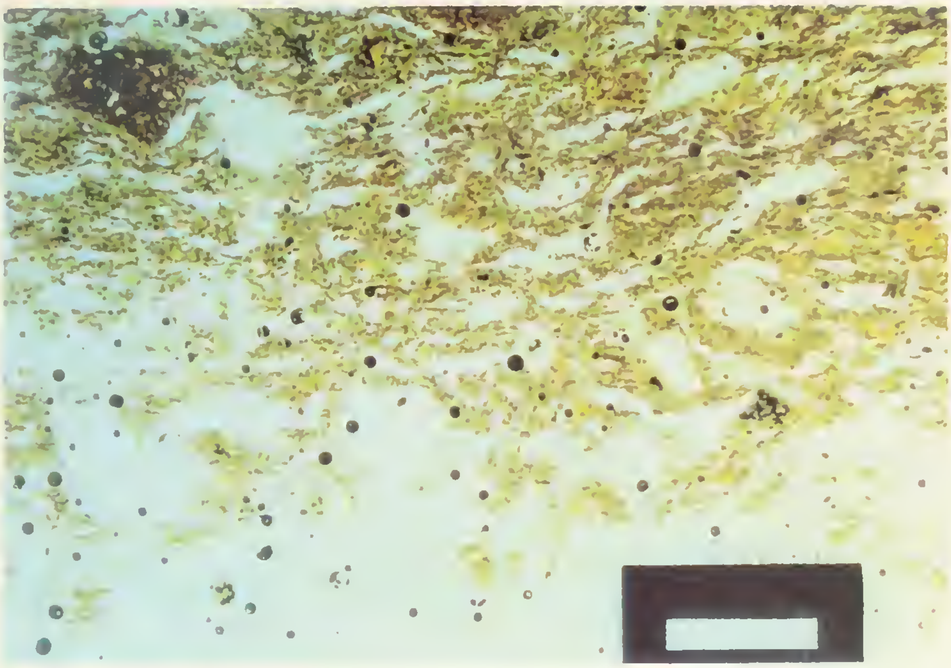
Treated Boston Valley sample at 25X, transmitted polarized light



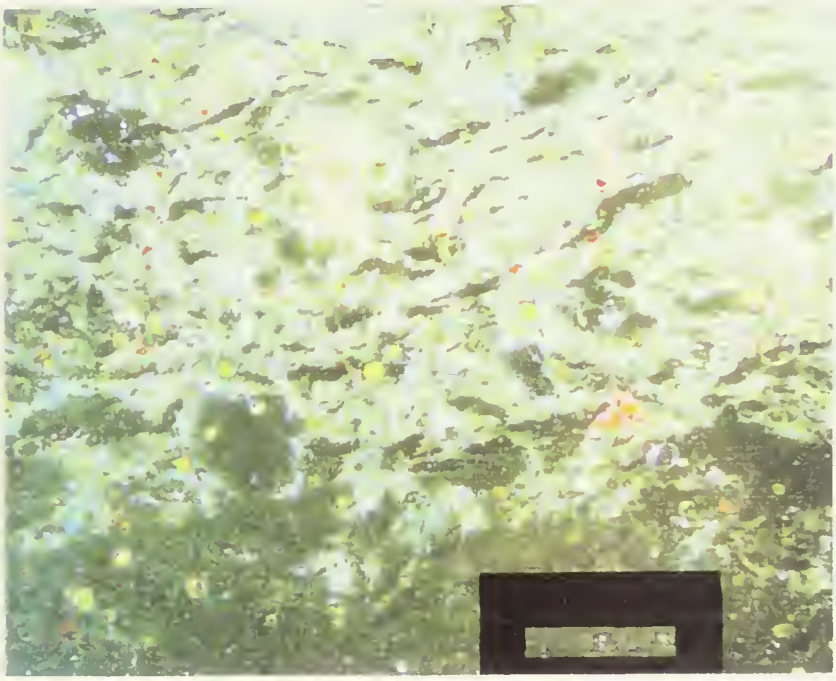
Untreated Boston Valley sample at 25X, transmitted light



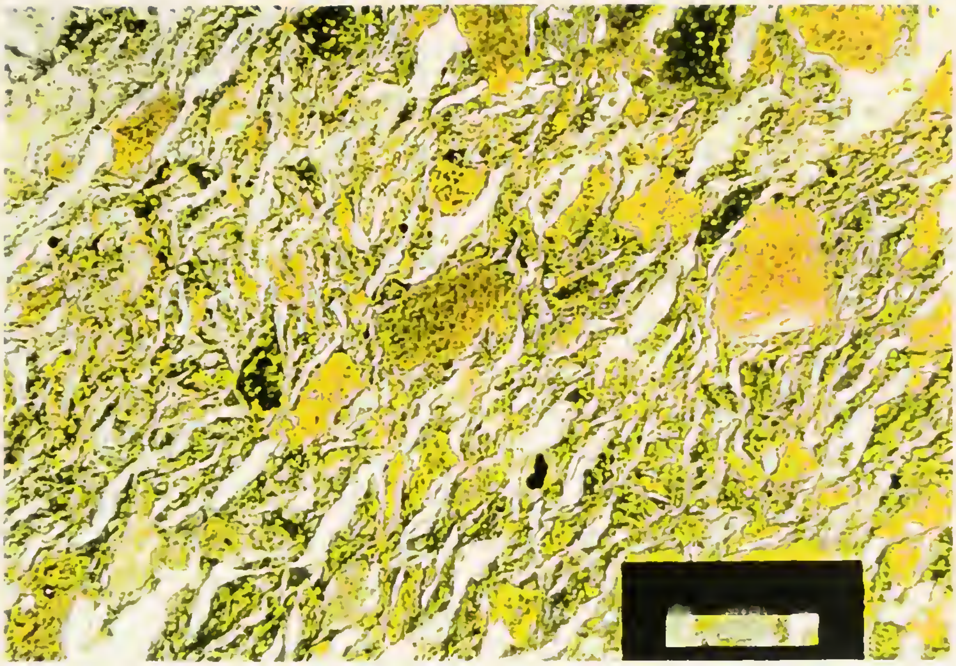
Untreated Boston Valley sample at 25X, transmitted polarized light



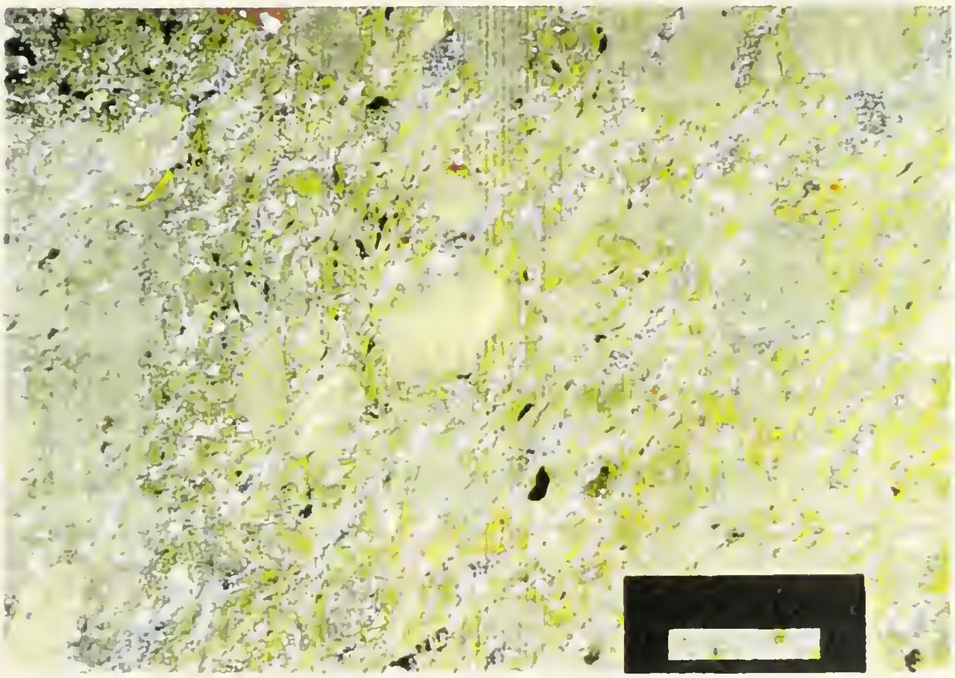
Treated Gladding, McBean sample at 25X, transmitted light



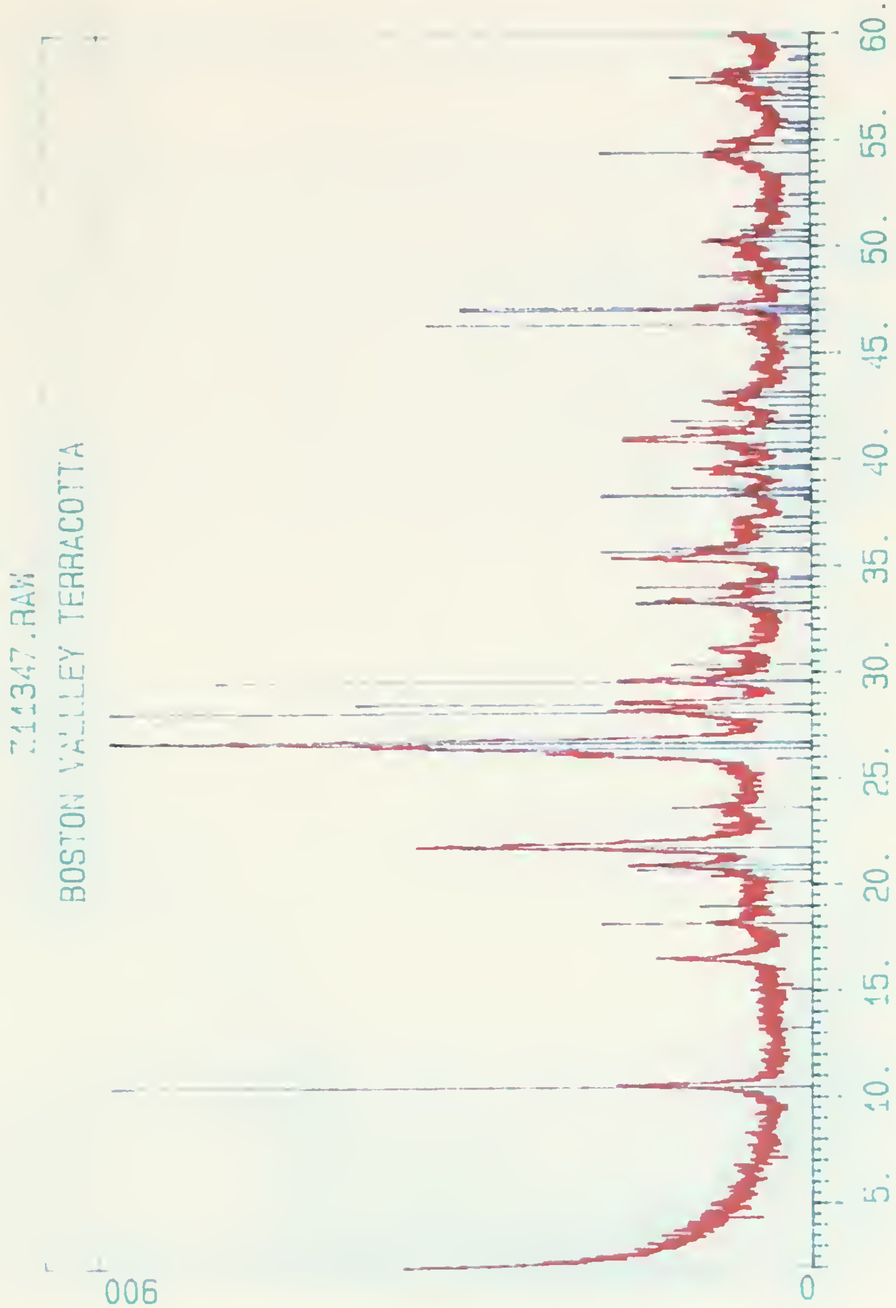
Treated Gladding McBean sample at 25X, transmitted polarized light



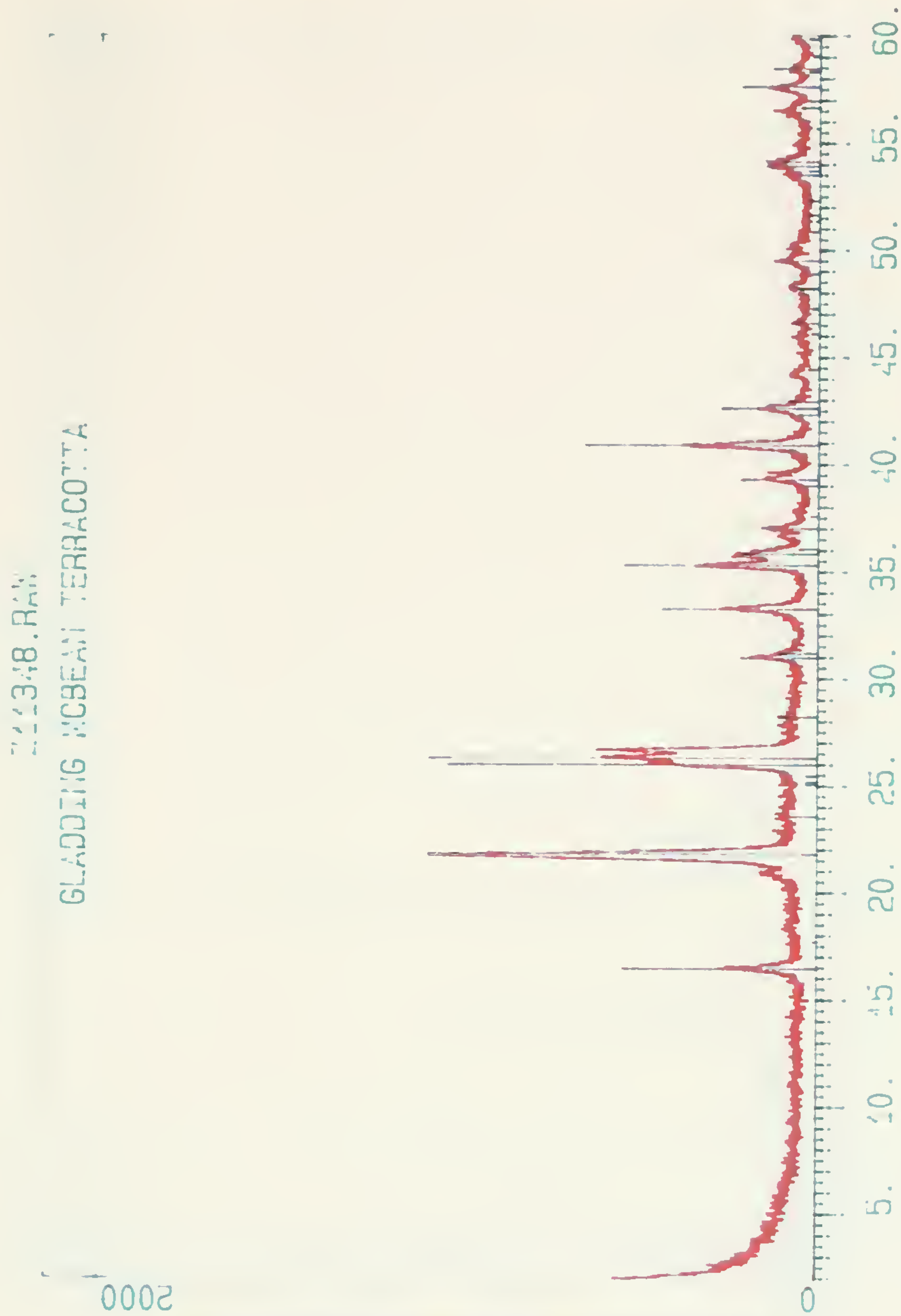
Untreated Gladding, McBean sample at 25X, transmitted light



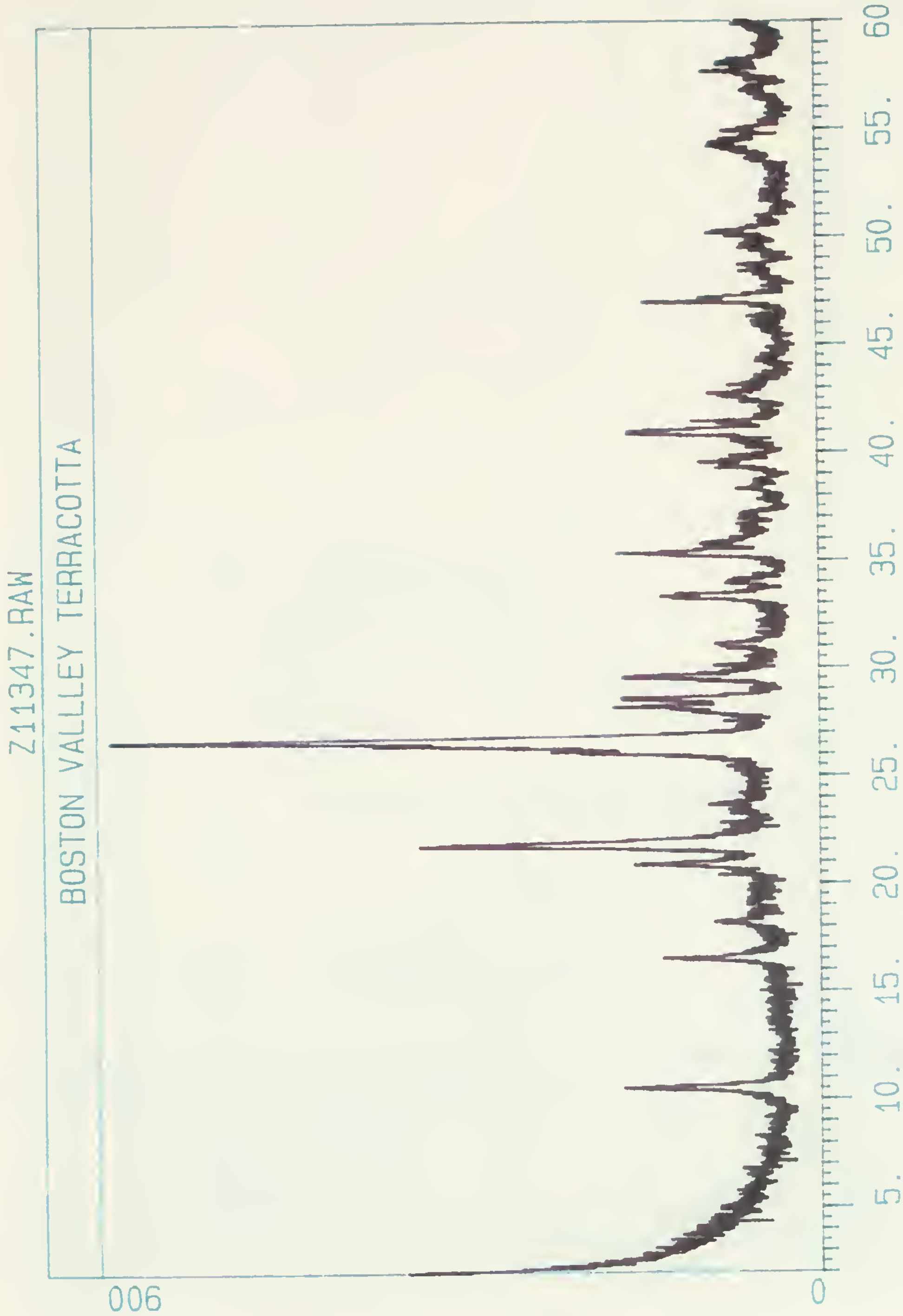
Untreated Gladding, McBean sample at 25X, transmitted polarized light

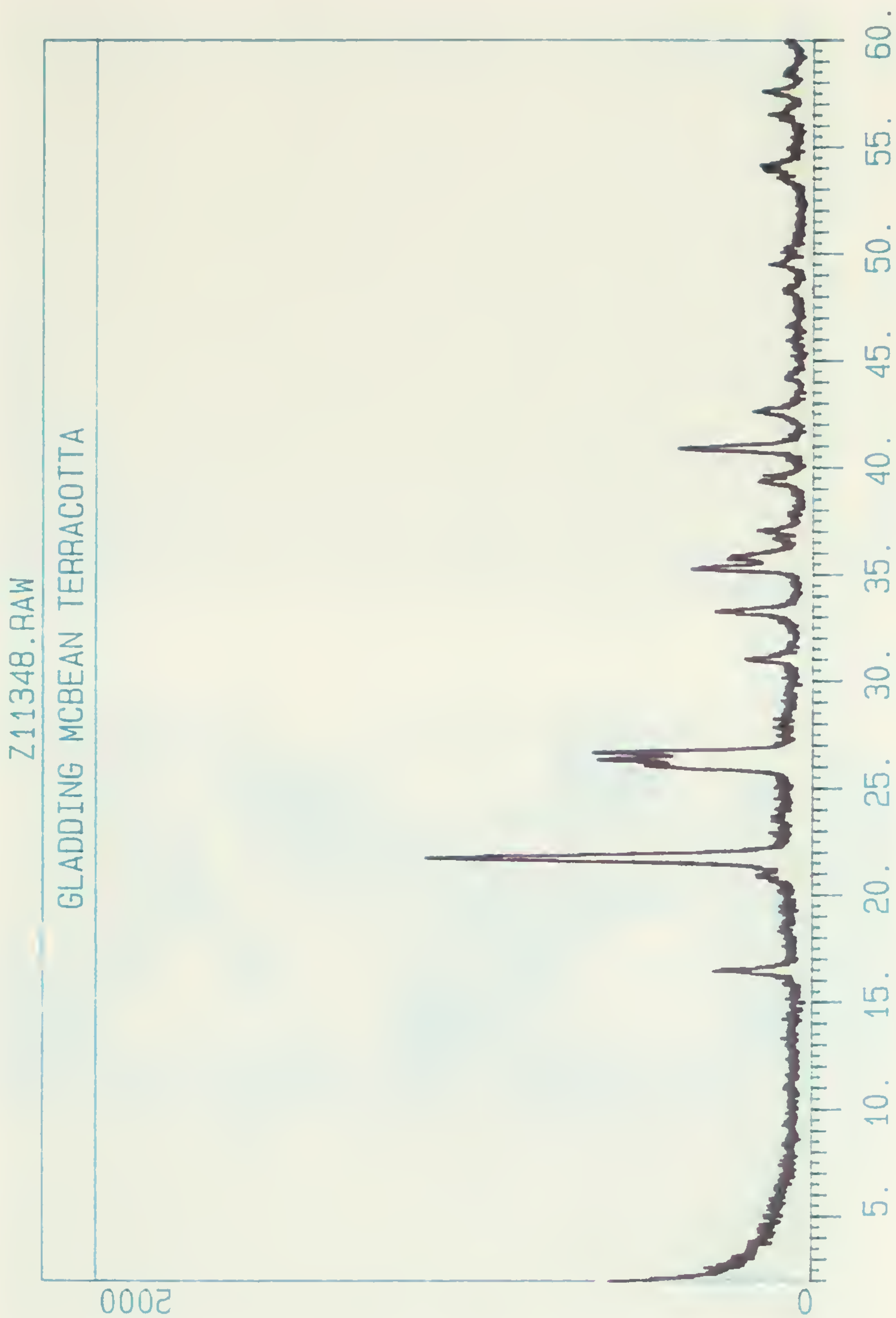


MINERAL NAME	PEAK COLOR
Indialite	violet
Mullite	yellow
Quartz	green
Kyanite	black



MINERAL NAME	PEAK COLOR
Mullite	violet
Aluminum Phosphate	green
Quartz	yellow


Z11347.RAW
BOSTON VALLLEY TERRACOTTA
900
0
5. 10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60.


Z11348.RAW
GLADDING MCBEAN TERRACOTTA
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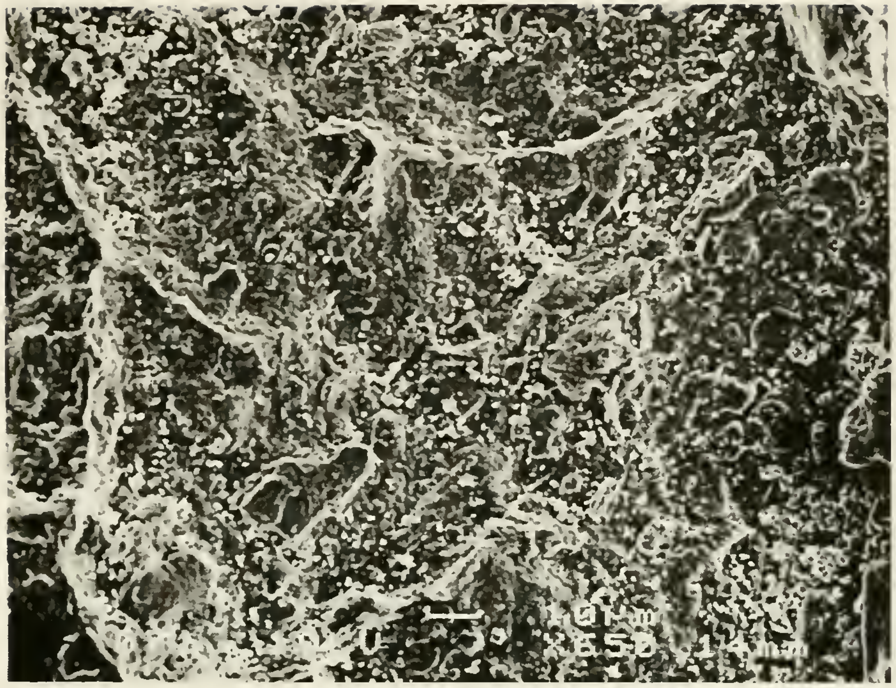
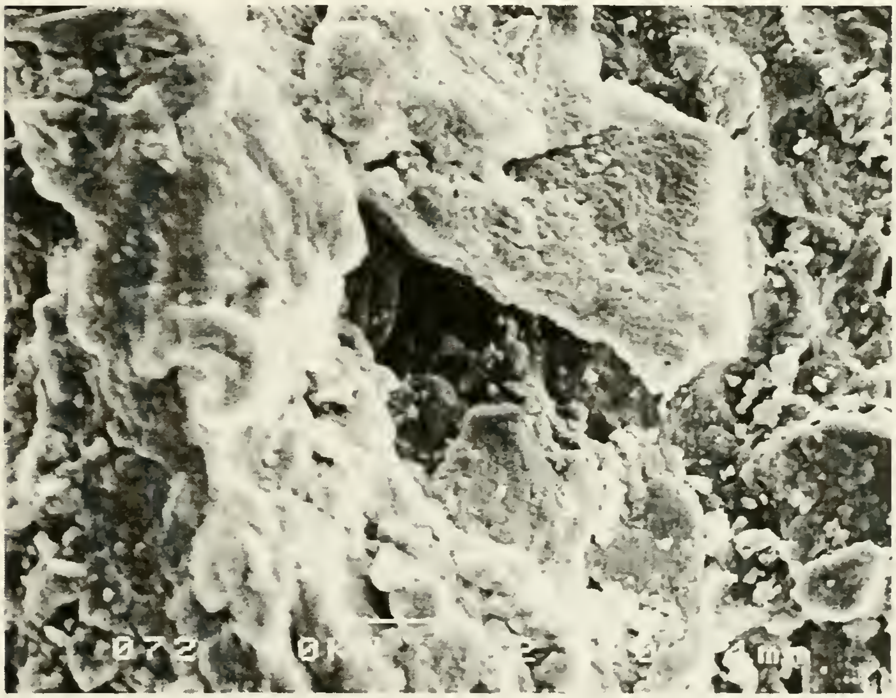
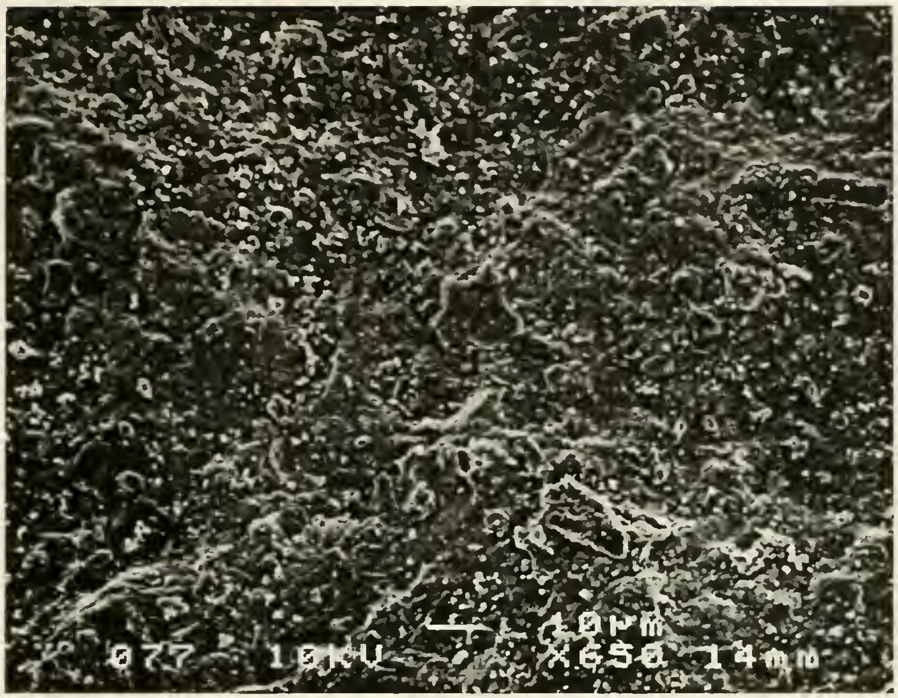
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.



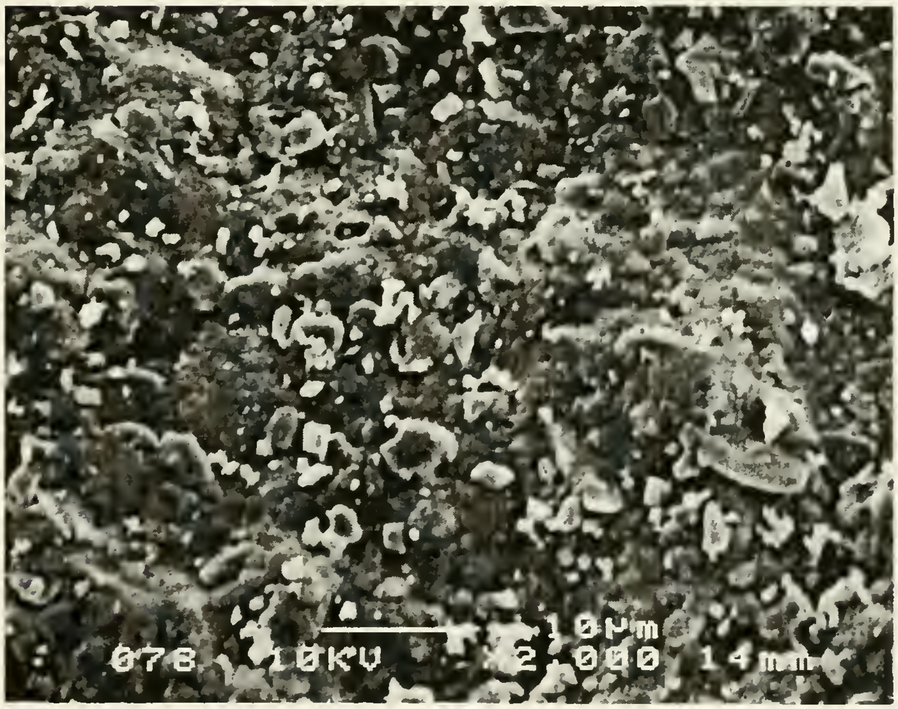
BV-01-0 at 650X



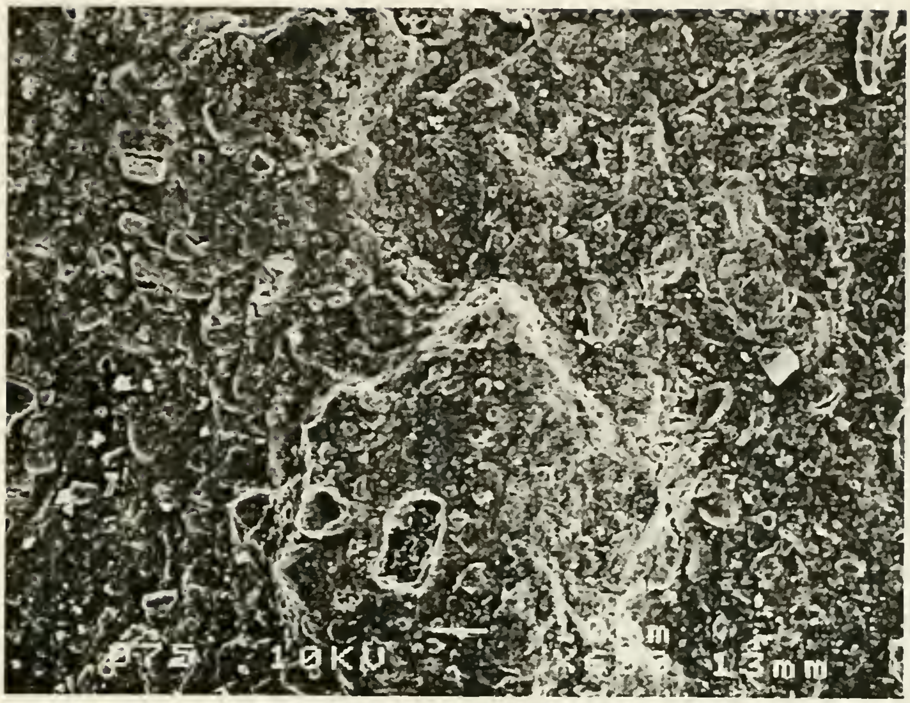
BV-01-0 at 2000X



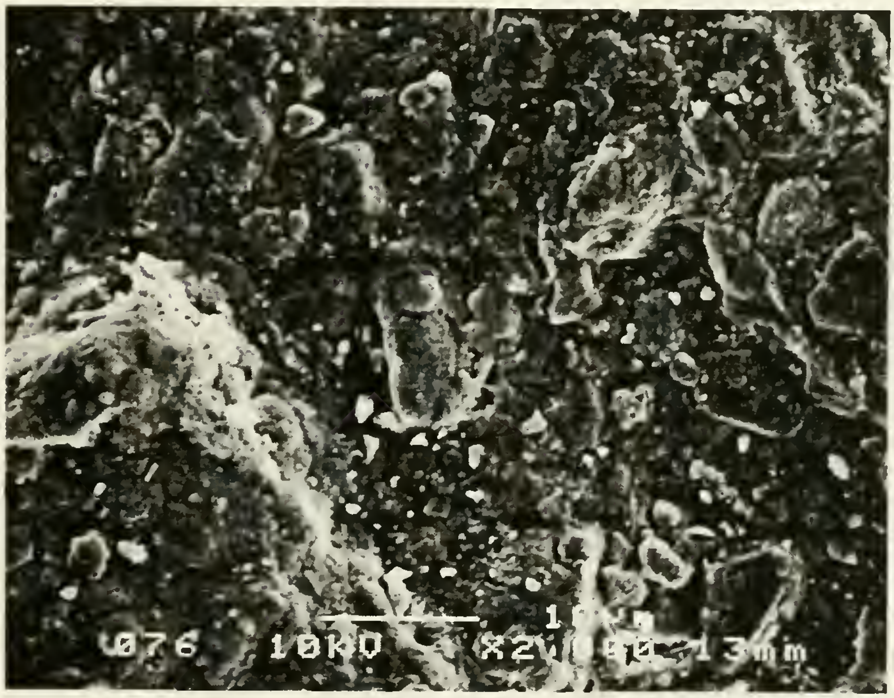
BV-01-1 at 650X



BV-01-1 at 2000X

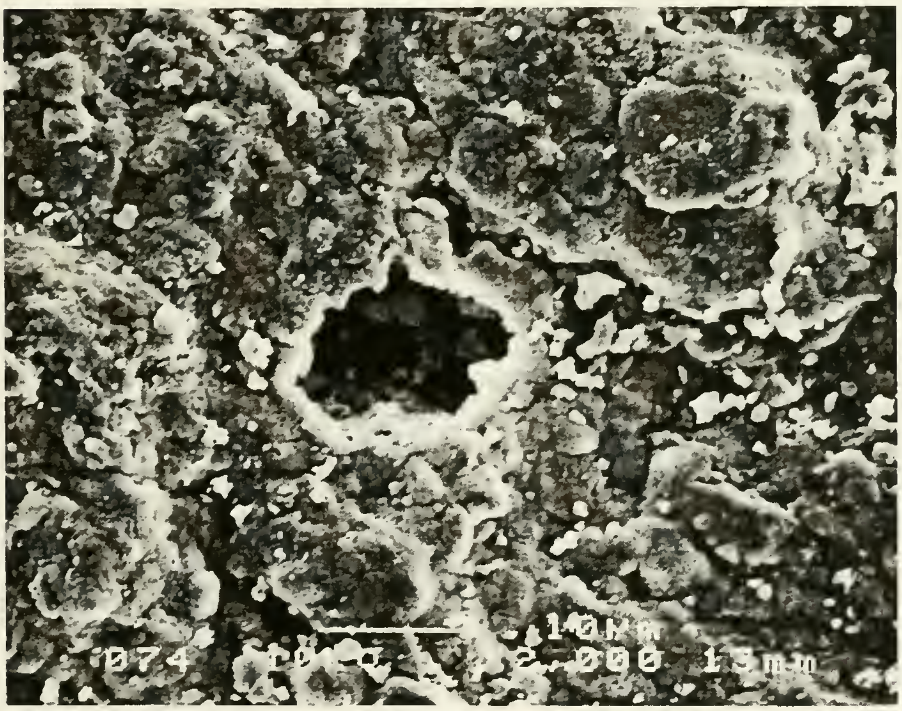


BV-01-2 at 650X

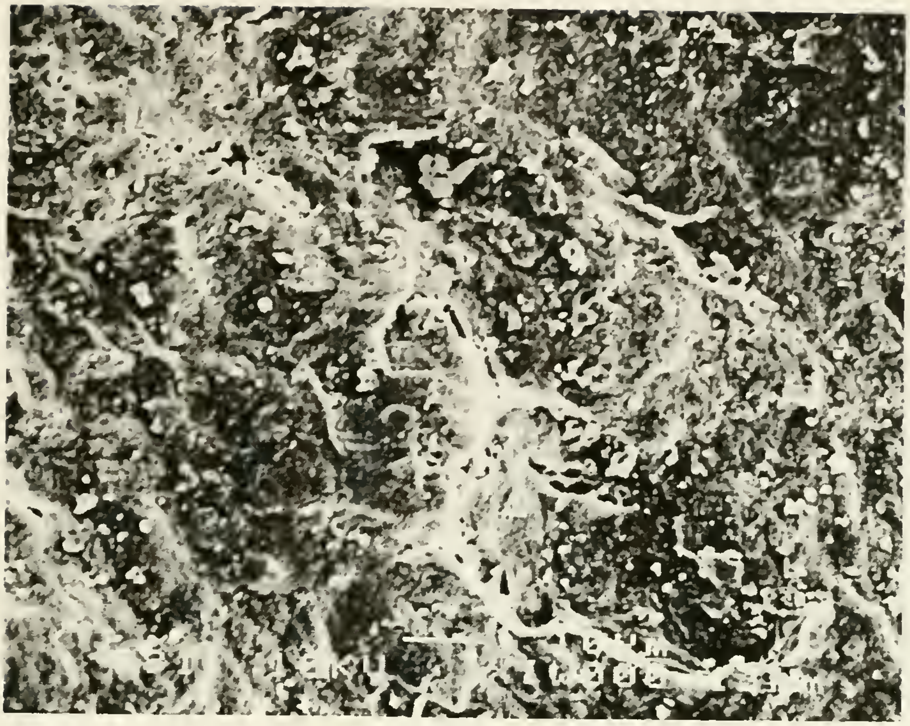


BV-01-2 at 2000X

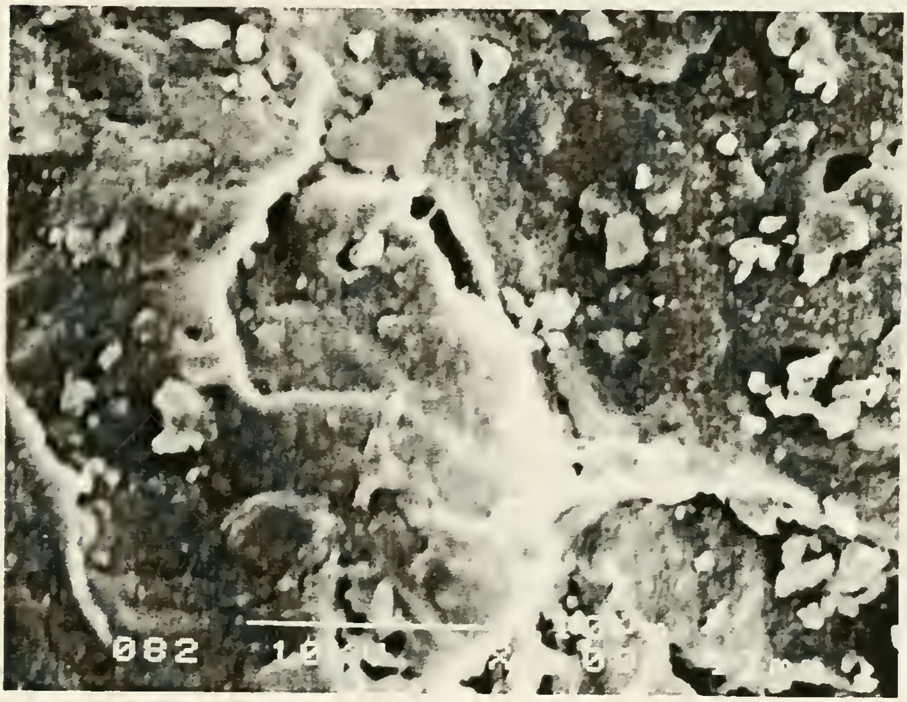
BV-01-3 at 650X



BV-01-3 at 2000X



GMB-01-0 at 1000X

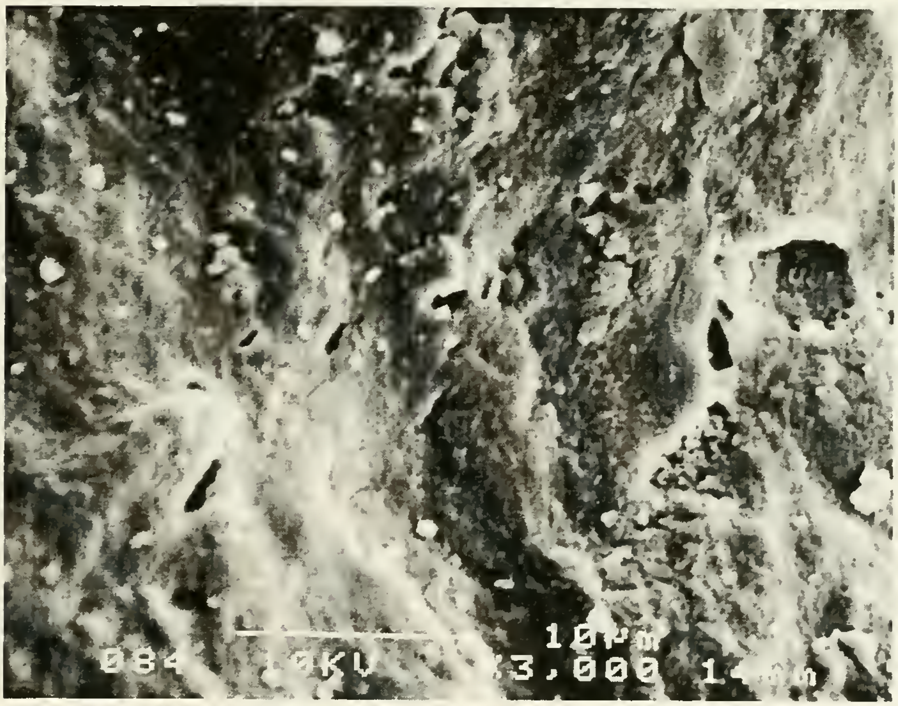


GMB-01-0 at 3000X

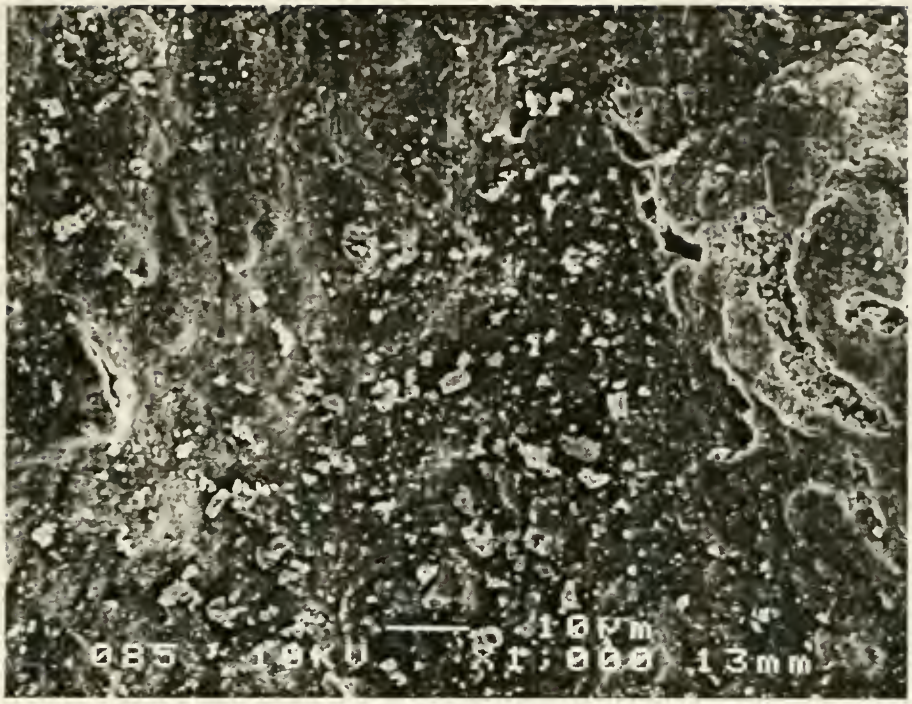
GMB-01-1 at 1000X

GMB-01-1 at 3000X

GMB-01-2 at 1000X

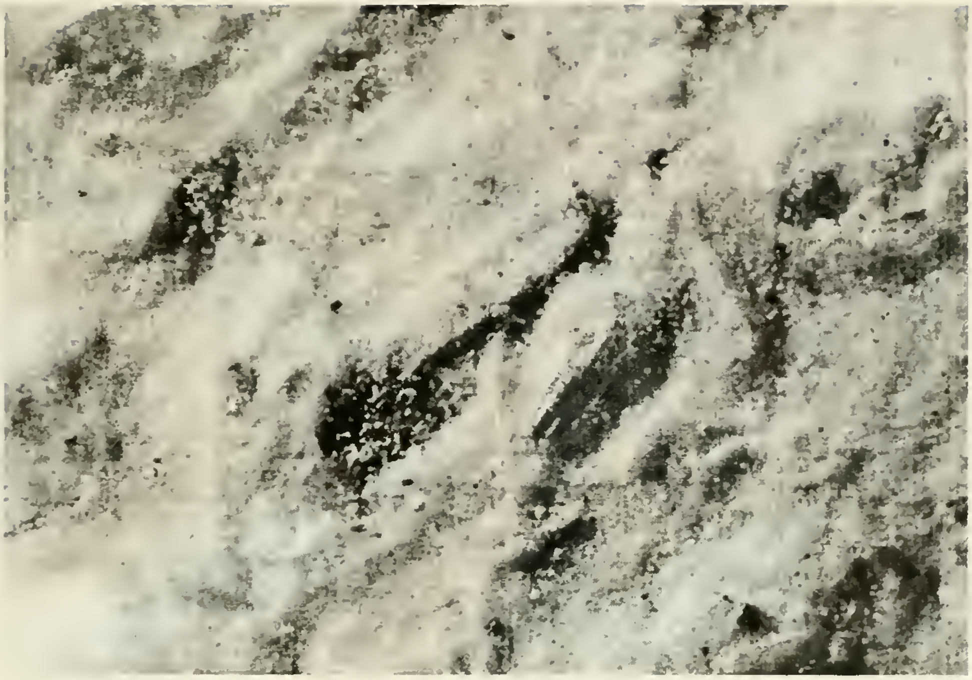


GMB-01-2 at 3000X

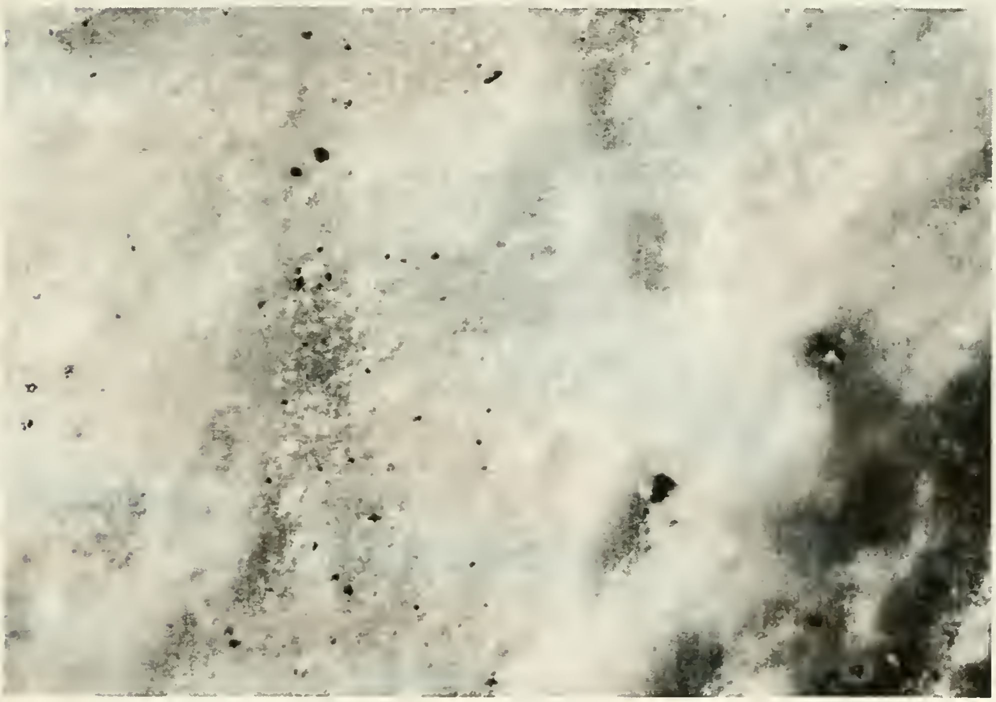


GMB-01-3 at 1000X

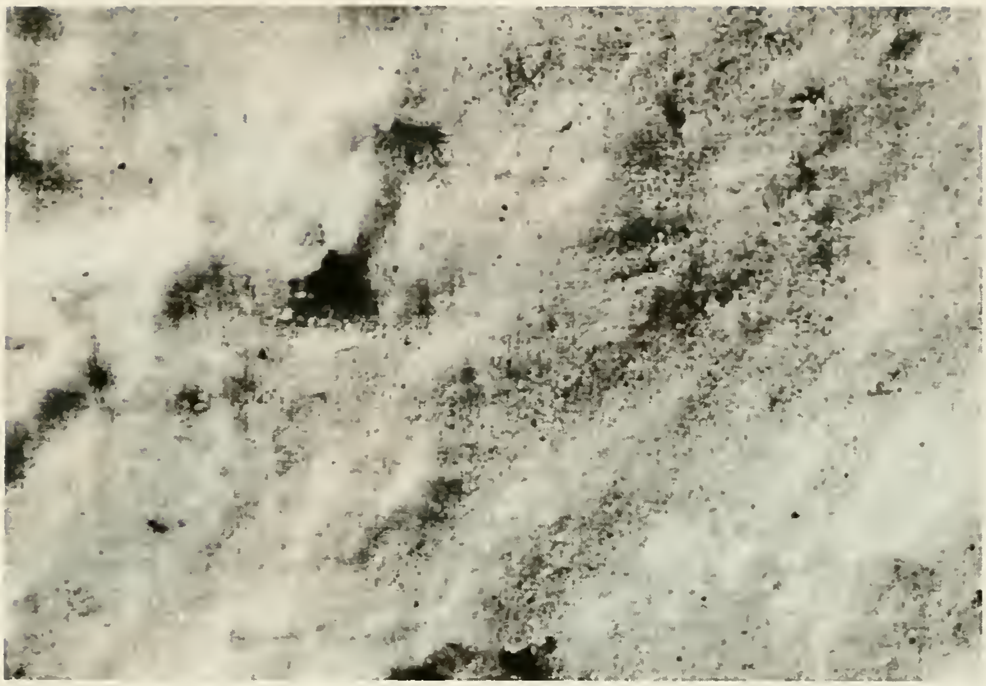
GMB-01-3 at 3000X



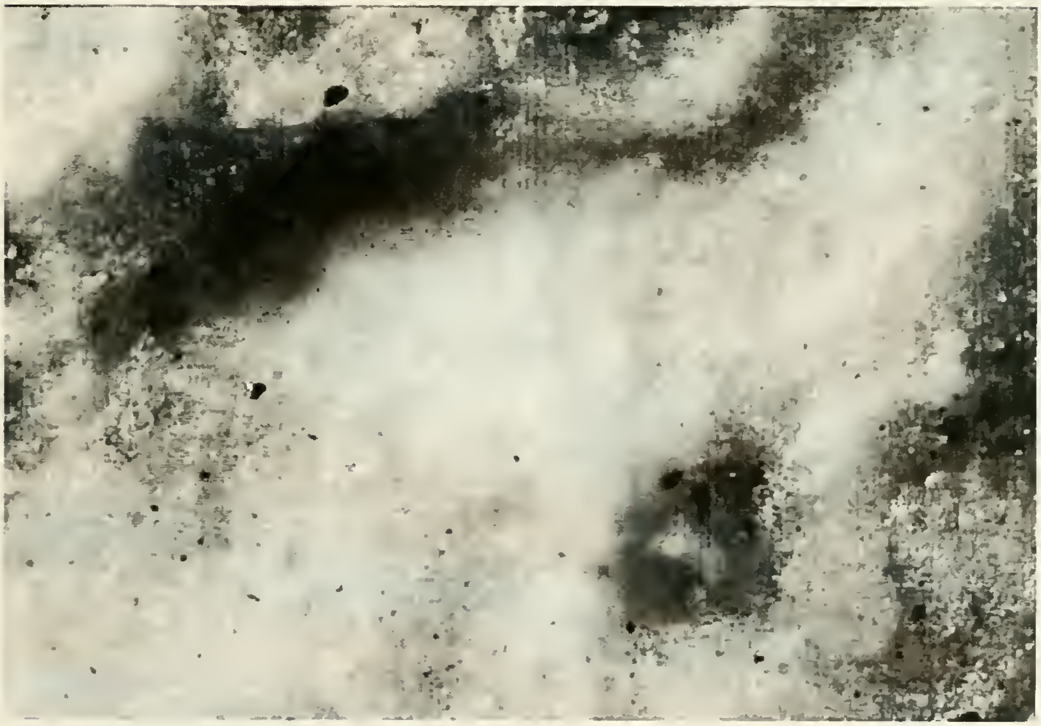
BV-01-0 at 40X



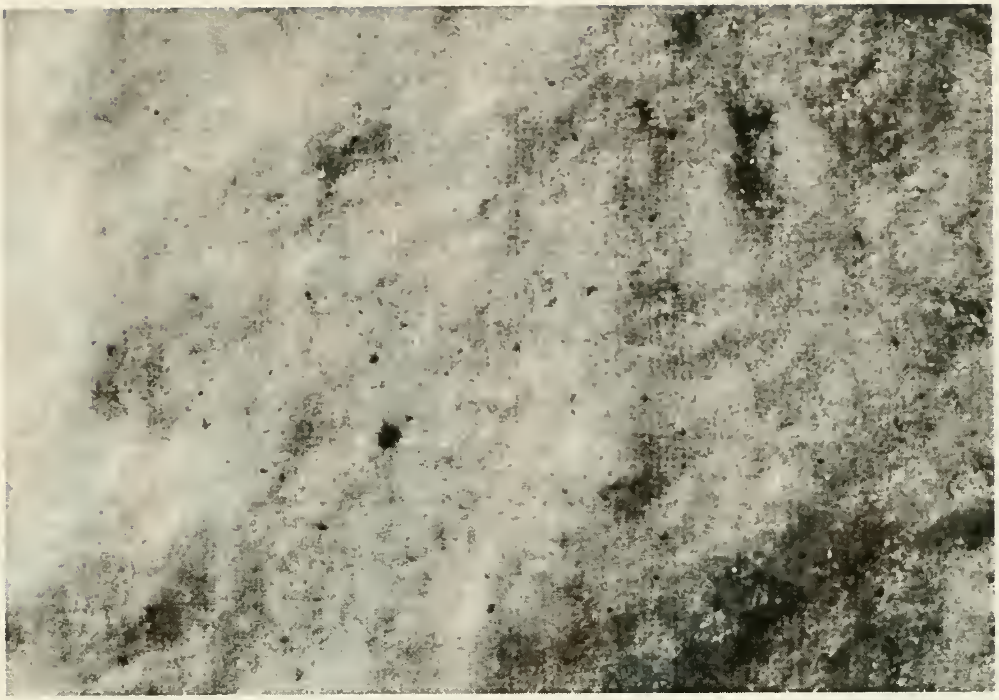
BV-01-0 at 100X



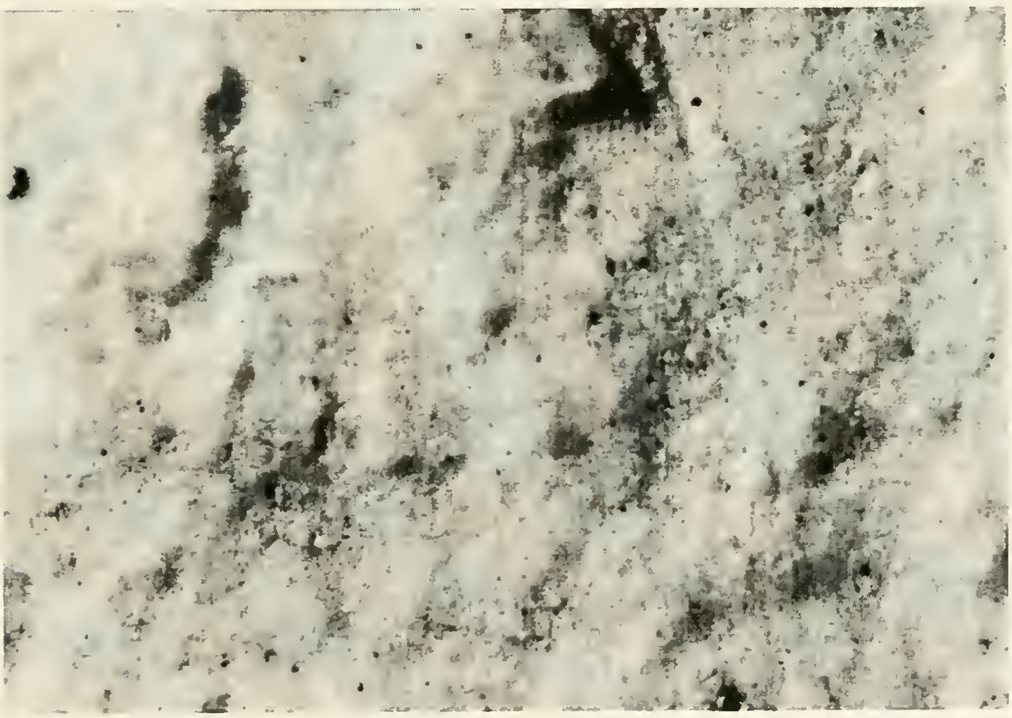
BV-01-1 at 40X



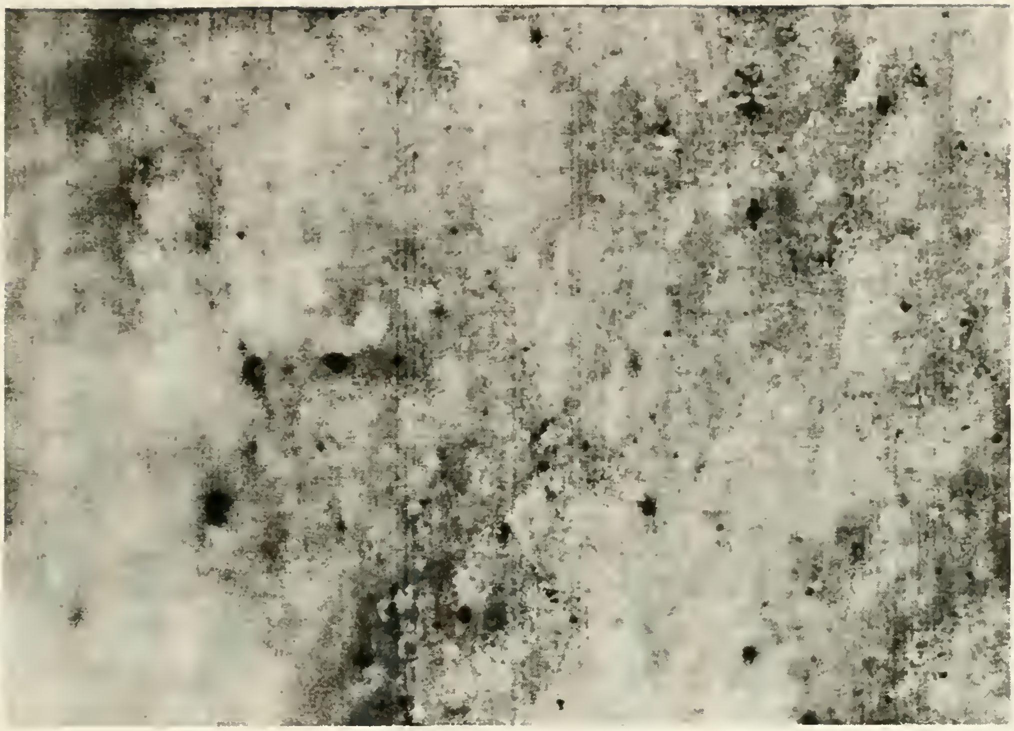
BV-01-2 at 100X



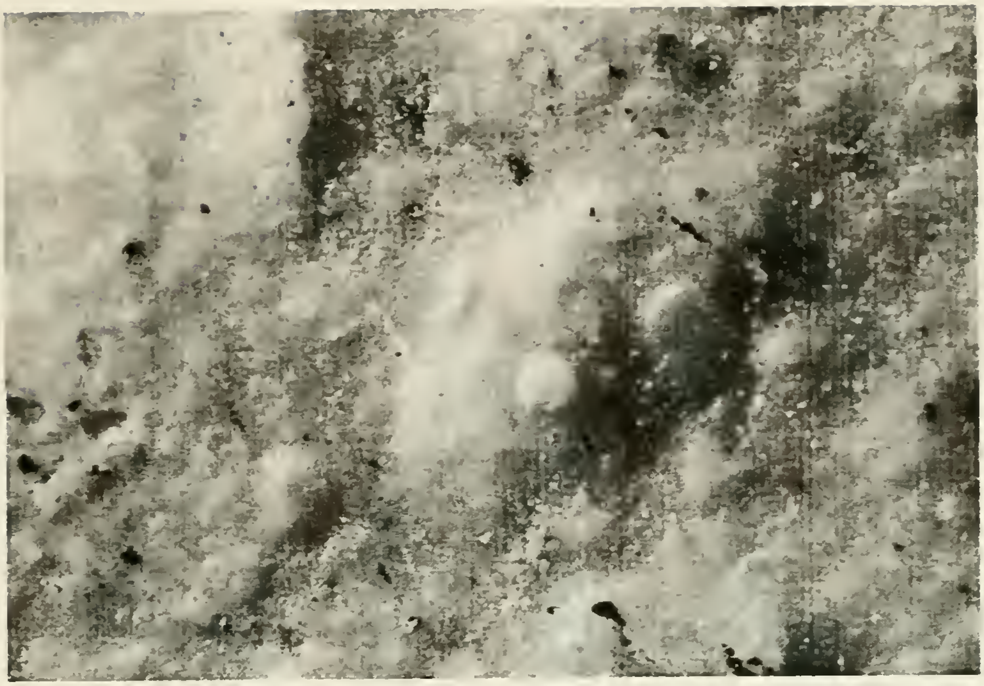
BV-01-2 at 40X



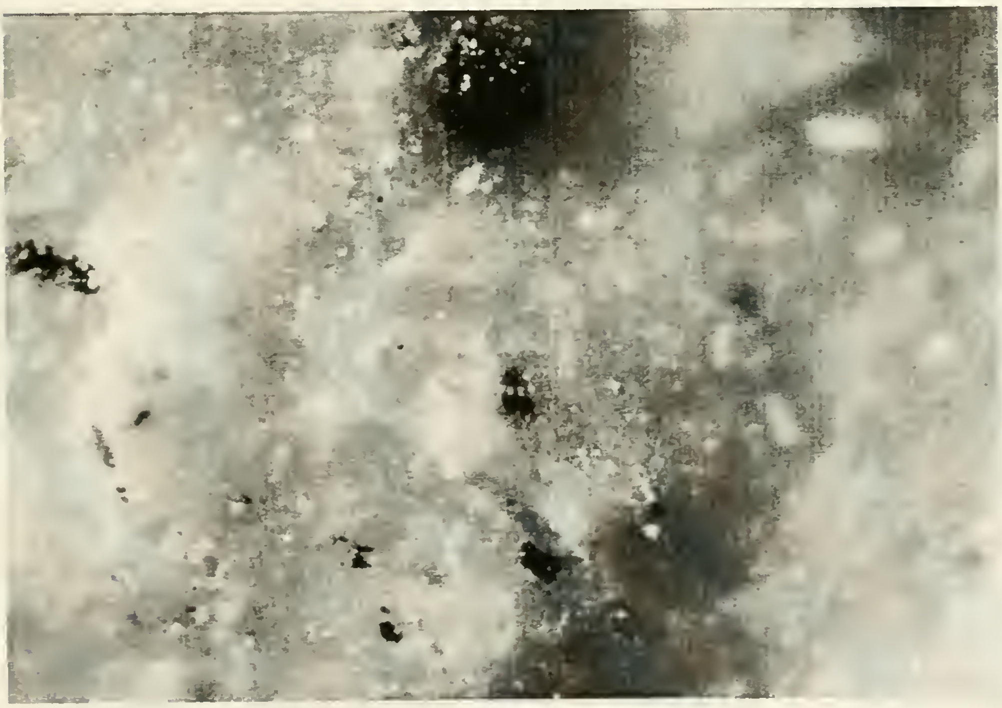
BV-01-2 at 100X



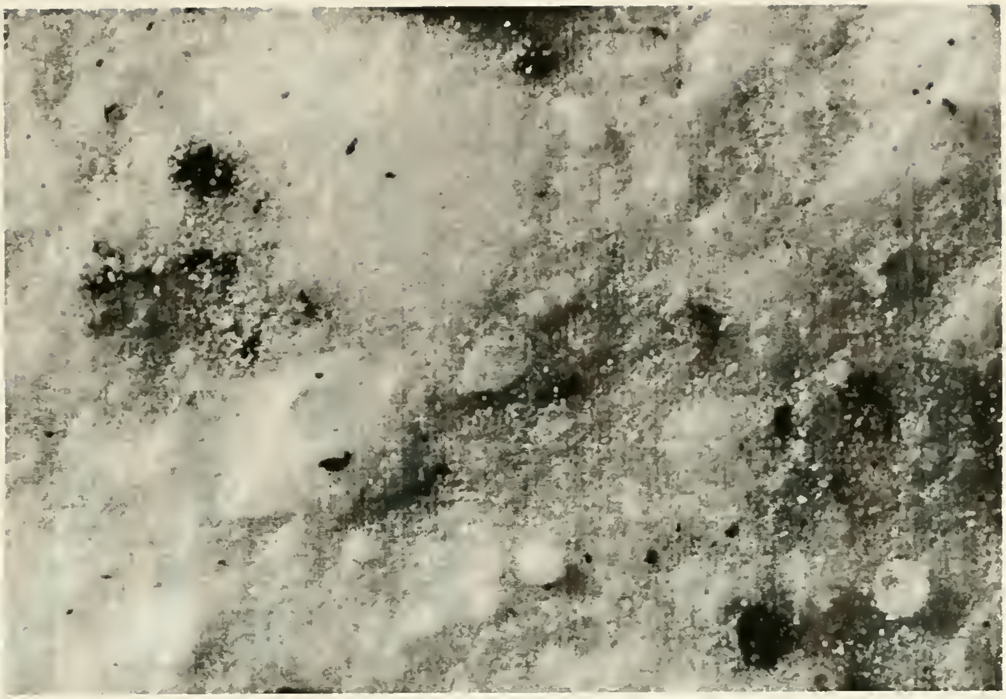
BV-01-3 at 100X



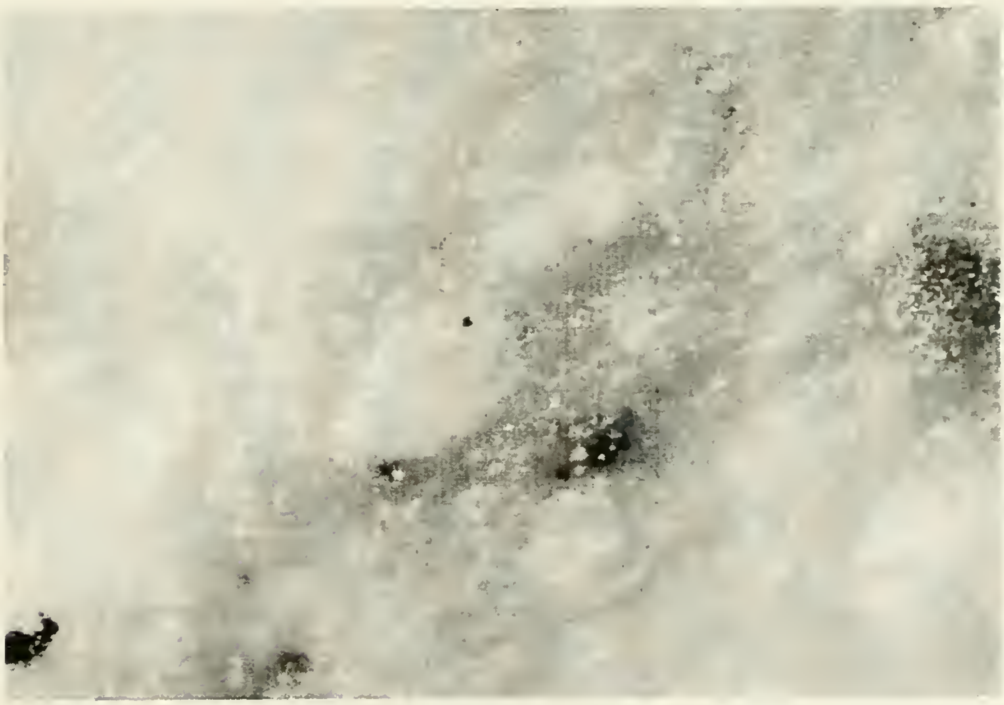
GMB-01-0 at 40X



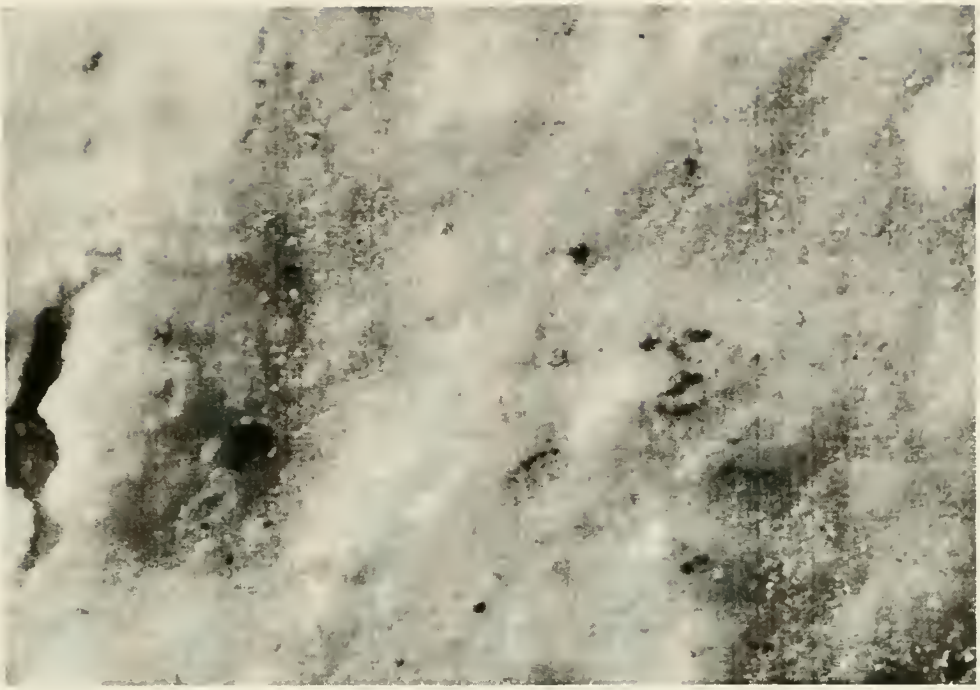
GMB-01-0 at 100X



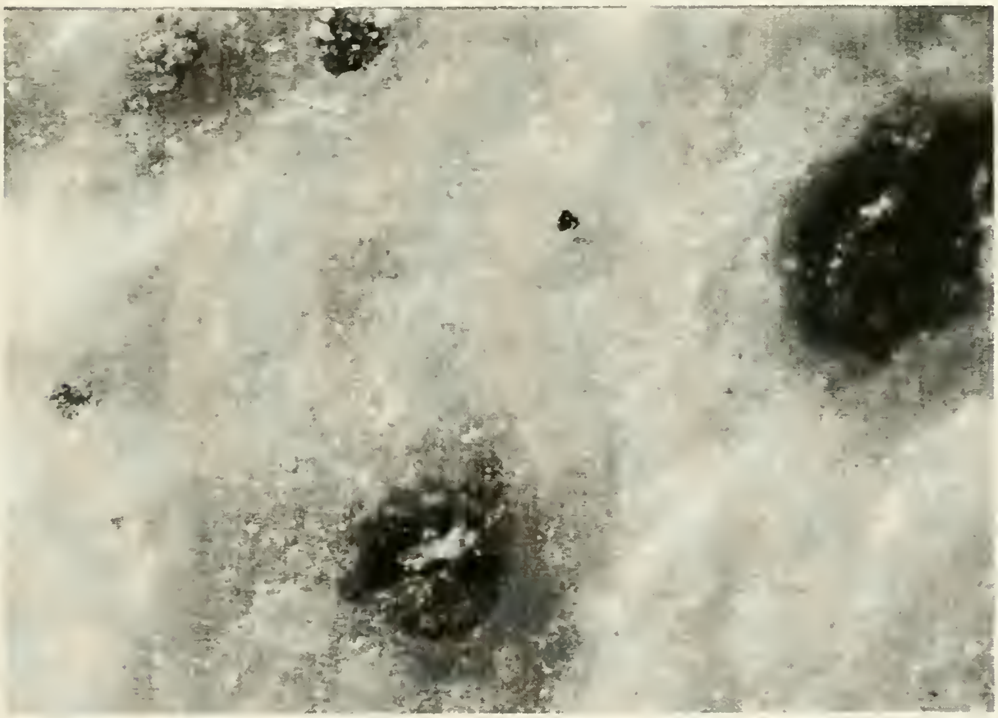
GMB-01-1 at 40X



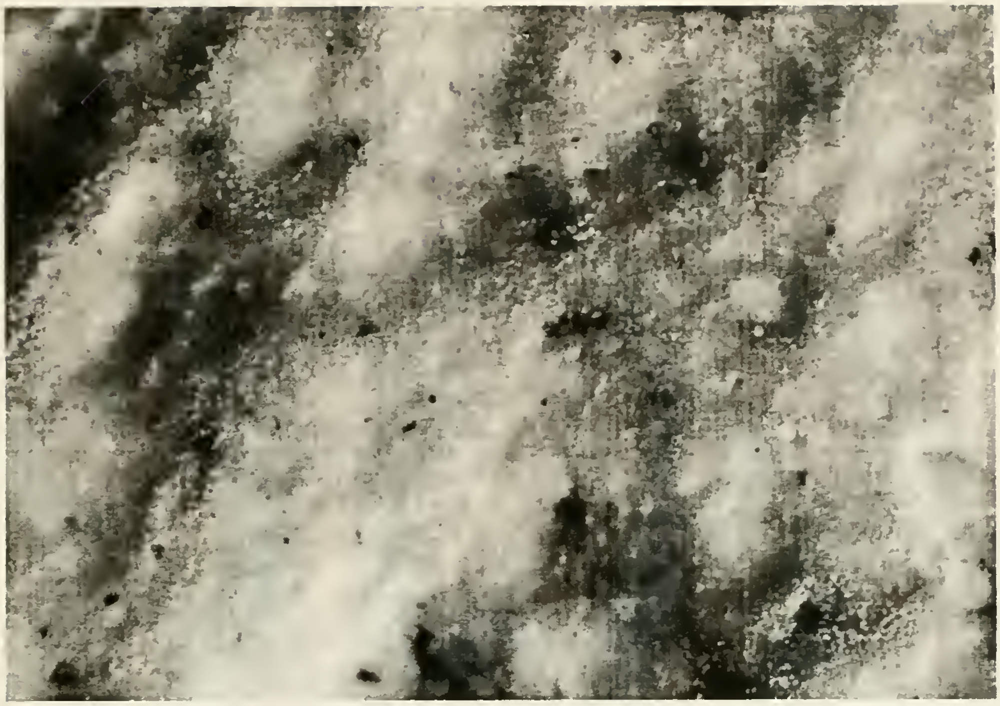
GMB-01-2 at 100X



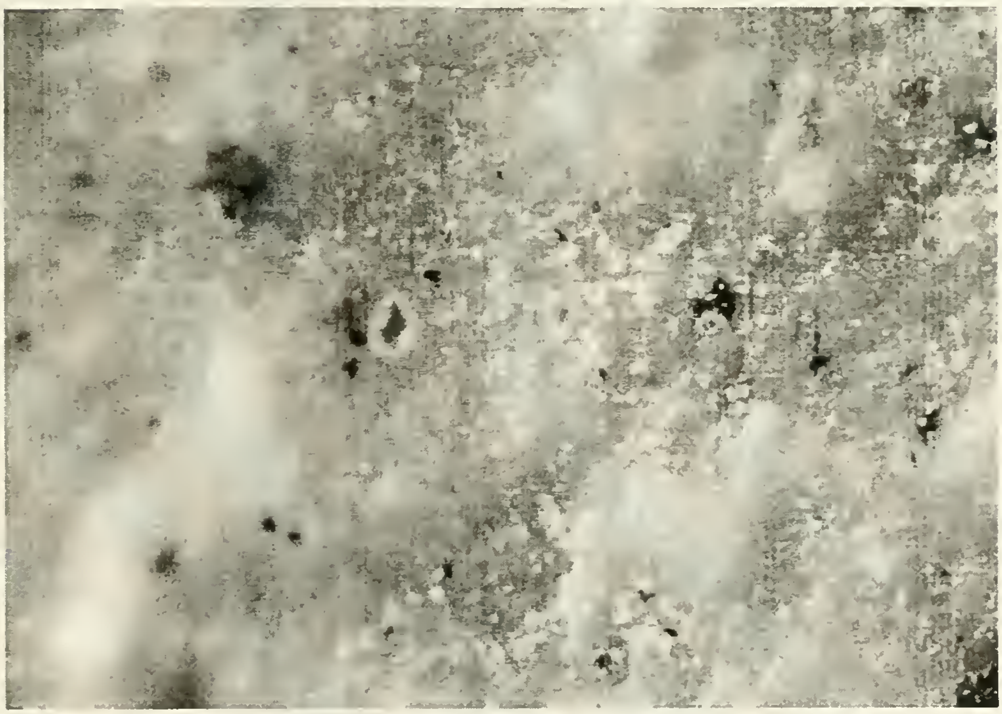
GMB-01-2 at 40X



GMB-01-2 at 100X



GMB-01-3 at 40X



GMB-01-3 at 100X

ISSUE	TESTING METHOD	SAMPLING SUMMARY					
		GLADDING, MCBEAN			BOSTON VALLEY		
How does Hydrofluoric acid-based cleaner affect the weathering potential of unglazed terracotta?	Crystallization of Salts	GMB-04-0	GMB-05-0	GMB-06-0	BV-04-0	BV-05-0	BV-06-0
		GMB-04-1	GMB-05-1	GMB-06-1	BV-04-1	BV-05-1	BV-06-1
		GMB-04-2	GMB-05-2	GMB-06-2	BV-04-2	BV-05-2	BV-06-2
		GMB-04-3	GMB-05-3	GMB-06-3	BV-04-3	BV-05-3	BV-06-3
	Freeze/Thaw	GMB-07-0	GMB-08-0	GMB-09-0	BV-07-0	BV-08-0	BV-09-0
		GMB-07-1	GMB-08-1	GMB-09-1	BV-07-1	BV-08-1	BV-09-1
		GMB-07-2	GMB-08-2	GMB-09-2	BV-07-2	BV-08-2	BV-09-2
		GMB-07-3	GMB-08-3	GMB-09-3	BV-07-3	BV-08-3	BV-09-3
	Accelerated Weathering	GMB-10-0	GMB-11-0	GMB-12-0	BV-10-0	BV-11-0	BV-12-0
		GMB-10-1	GMB-11-1	GMB-12-1	BV-10-1	BV-11-1	BV-12-1
		GMB-10-2	GMB-11-2	GMB-12-2	BV-10-2	BV-11-2	BV-12-2
		GMB-10-3	GMB-11-3	GMB-12-3	BV-10-3	BV-11-3	BV-12-3

ISSUE	TESTING METHOD	SAMPLING SUMMARY					
		GLADDING, MCBEAN			BOSTON VALLEY		
What methods can be used to quantify the changes caused by hydrofluoric acid based cleaning?	SEM/Zidas	GMB-01-0	GMB-02-0	GMB-03-0	BV-01-0	BV-02-0	BV-03-0
		GMB-01-3	GMB-02-3	GMB-03-3	BV-01-3	BV-02-3	BV-03-3
	Porosity	GMB-02-0	GMB-03-0		BV-02-0	BV-03-0	
		GMB-02-1	GMB-03-1		BV-02-1	BV-03-1	
		GMB-02-2	GMB-03-2		BV-02-2	BV-03-2	
		GMB-02-3	GMB-03-3		BV-02-3	BV-03-3	
	Permeability	GMB-13-0	GMB-14-0	GMB-15-0	BV-13-0	BV-14-0	BV-15-0
		GMB-13-3	GMB-14-3	GMB-15-3	BV-13-3	BV-14-3	BV-15-3
	Touch Test Assessment	GMB-02-0	GMB-03-0		BV-02-0	BV-03-0	
		GMB-02-1	GMB-03-1		BV-02-1	BV-03-1	
		GMB-02-2	GMB-03-2		BV-02-2	BV-03-2	
		GMB-02-3	GMB-03-3		BV-02-3	BV-03-3	
	Water Drop Absorption	GMB-02-0	GMB-03-0		BV-02-0	BV-03-0	
		GMB-02-1	GMB-03-1		BV-02-1	BV-03-1	
		GMB-02-2	GMB-03-2		BV-02-2	BV-03-2	
		GMB-02-3	GMB-03-3		BV-02-3	BV-03-3	

Abrate-Zohar, M.A., et al. "Decay Stage and Causes of the Terracotta Ornaments." *Proceedings of the Fifth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985.* Lausanne: Presses Polytechniques Romandes, 1985, 443-451.

A case that evaluates the deterioration of fifteenth century terra cotta statuary in an Italian cloister. Ultimately, gypsum originating from deterioration of calcite in mortars is blamed for deterioration in terracotta.

Adams, Eric. "Collaborating With Conservators." *Architecture* 1997 (86:9, 138-44).

Discussion of the roles of the architects and conservators in the conservation of glazed terracotta.

Alessandrini, Giovanna, and A.M. Bocci, B. Fabbri, G. Ercolani. "Decorative Terra Cotta Inside the Cappella Portinari; their composition and decay." *Ceramics in Architecture. ed. P. Vicenzini. Proceedings of the International Symposium The Ceramics Heritage of the 8th Cimtec World Ceramics Congress and Forum on New Materials, Florence, Italy, June 28-July 2, 1994.* Faenza: Techna, 1995. 551-560.

Antunes, J.L., M.O. Figueiredo, J. Costa Pessoa, and M. Ammaral Fortes. "Characterization of Portuguese 17th century tiles." *The Ceramics Cultural Heritage, ed. P. Vicenzini. Proceedings of the International Symposium The Ceramics Heritage of the 8th Cimtec World Ceramics Congress and Forum on New Materials, Florence, Italy, June 28-July 2, 1994.* Faenza: Techna, 1995. 653-660.

As the title indicates, this is primarily a characterization of ceramic tiles. Methods employed include XRD, SEM, and XRF. An immersion technique for desalinization is evaluated.

Ashurst, John and Nicola. *Brick, Terracotta, and Earth,* volume 2 of *Practical Building Conservation, English Heritage Technical Handbook Series.* Aldershot: Gower Publishing, 1988.

This is an excellent sourcebook on terracotta. It defines terra cotta and gives a brief history of the use of the material and a summary of the manufacturing process. Discusses patterns and causes of deterioration, cleaning methods, and strategies for general repair and maintenance.

Ashurst, John. "Cleaning and Surface Repair: Past Mistakes and Future Prospects." *APT Bulletin* 1985 (17:2, 39-41).

Assesses effects of several cleaning systems on buildings in urban areas 10-15 years post-cleaning. Suggests improvements for training and assessment.

Ashurst, John. "Cleaning Stone and Brick." *Technical Pamphlet 4.* London: Society for the Protection of Ancient Buildings, 1977.

Evaluates masonry cleaning methods including washing, abrasive blasting, chemical cleaning, mechanical cleaning, and selection of method. Views are outdated.

Ashurst, Nicola. *Cleaning Historic Buildings.* 2 volumes. London: Donhead Publishing, 1994.

Cleaning sourcebook. Comprehensive description of soiling, substrates, and cleaning techniques.

Baer, N.S., and R. Snethlage. *Saving Our Architectural Heritage: the Conservation of Historic Stone Structures.* New York: John Wiley and Sons, 1997.

A collection of reports and articles regarding conservation of stone. Topics include the ethical considerations of conservation treatments, methods of evaluating treatments, interpretation of field testing, risk to architectural heritage, aspects of economic valuation of architectural heritage.

Barrenche, Raul A. "Restoring Terra-Cotta." *Architecture* 1994 (83:11, 127-133).

Restoration of glazed terra cotta.

Berryman, Nancy and Susan Tindall. *Terracotta.* Chicago: Landmarks Council of Illinois, 1984.

This is a good basic source on terracotta. It touches briefly on many topics, and explains the manufacturing process well.

Bradt, R.C. (ed.). *Fracture Mechanics of Ceramics,* Vol. 5. New York: Plenum Press, 1983.

This is a technical book on fracture mechanics aimed at engineers.

Brereton, Christopher. *The Repair of Historic Buildings: Advice on Principles and Methods.* London: English Heritage, 1991.

Basic advice on the repair of historic buildings.

Bristow, Alan J. "Renovating Terracotta Work on Birmingham's Central Mission." *Building Conservation* 1981 (3:6, 10-12).

This is a case study on terra cotta renovation project.

Building Research Establishment. "Design and appearance , 1-2." *Building Defects and Maintenance: Essential Information from the Building Research Establishment.* Lancaster: The Construction Press, 1974, 2-13.

This article presents the aesthetic argument--the impact that soiling has on the visual interpretation of a building.

Casadio, R. et al. "The Deterioration of 'Terracotta:' the Case of Casa Valenti in Faenza." *Science, Technology, and European Cultural Heritage: Proceedings of the European Symposium, Bologna, Italy, 13-16 June 1989.* Guildford: Butterworth-Heinemann, 1991. 894-899.

Despite identical exposure and micro-climate, certain masonry units of Casa Valenti are deteriorating preferentially. Ultimately, the author concluded that some blocks were insufficiently fired, resulting in preferential deterioration.

Celoria, Francis. "Contributions Toward a Working Definition of Terracotta." *Journal of the Tiles and Architectural Ceramics Society* 1987 2: 10-20.

Glossary of different definitions of terracotta; this article highlights the difficulty of arriving at a single definition of terracotta.

Charola, A. Elena, Carol A. Grissom, Evin Erder, Melvin Wachowiak, and Douglas Oursler. "Measuring Surface Roughness: Three Techniques." *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone*, ed. Joseph Riederer. Berlin, 30 September - 4 October 1996, 1421-1434.

Evaluates three techniques of assessing surface roughness; laser triangulation profilometry, stylus profilometry, and reflected light image analysis. Laser triangulation profilometry and reflected light image analysis required replicas of the surface.

Clifton, James R. *Cleaning Stone and Masonry: a symposium.* ASTM Special Publication 935. Philadelphia: ASTM, 1986.

This is a compilation of articles regarding selection of appropriate methods and materials for cleaning, the cleaning of historic buildings, and determining the effects of cleaning.

Colombo, Chiara; Negrotti, Riccardo; Toniolo, Lucia; and Fabbri, Bruno. "The Ca Grande in Milan: The ceramic material and the oxalate films." *Proceedings of the International symposium (II) the oxalate films in the conservation of works of art, Milan, March 25-27, 1996.* Pages 189-205.

Crafts Council Conservation Science Teaching Series. *Cleaning.* Volume 2 of the *Science for Conservators Series*. London: Crafts Council, 1984.

An excellent source on the science behind the processes of cleaning. The nature of dirt and how it adheres to the sunstrate is discussed.

Croce, Cinzia, and Andreina Draghi, Renato Pennino, and Antonio Villarini. "The Restoration of Terra Cotta on the Façade of Saint Chiara in Rome." *The Ceramics Cultural Heritage, ed. P. Vicenzini. Proceedings of the International Symposium The Ceramics Heritage of the 8th Cimtec World Ceramics Congress and Forum on New Materials, Florence, Italy, June 28-July 2, 1994.* Faenza: Techna, 1995. 691-702.

Focuses on the history of the site. Deterioration of the statuary was blamed on improper firing, most likely the result of inexperience on the part of the firing technician.

Davis, Charles. *A Practical Treatise on the Manufacture of Brick, Tiles, and Terra Cotta.* Third edition. Philadelphia: Henry Carey Baird, 1895.

Discusses the manufacturing process of brick and architectural terra cotta in tremendous depth. Describes components and their effect on the properties of the finished material. An excellent resource.

Dinsdale, Allen. *Pottery Science: Materials, Processes, and Products.* Chichester: Ellis Horwood, Ltd. 1986.

Materials Science: discusses porosity, strength, and processes of firing.

Feller, Robert L. *Accelerated Aging: Photochemical and Thermal Aspects.* Ann Arbor: Research in Conservation Series, Edwards Bros, 1994.

Discusses the science of accelerated aging, processes, objectives, etc.

Fidler, John. "The Manufacture of Architectural Terracotta and Faience in the United Kingdom." *APT Bulletin* 1983 (15:2, 27-32).

History of the manufacturing process in the U.K.

Fidler, John. "The Conservation of Architectural Terra Cotta and Faience." *Transactions of the Association for Studies in the Conservation of Historic Buildings* 1981 (6: 3-16).

This is the first of a series of articles that are virtually identical, but have changed slightly over the years to reflect new knowledge and trends. It was reprinted in many sources: Friends of Terracotta Newsletter, SPAB news, and Teutonico's Architectural Ceramics. Includes a history of terra cotta from antiquity to the present, summarizes the manufacturing process, discusses deterioration mechanisms, soiling, cleaning techniques and methods of conservation.

Fidler, John. "The Conservation of Architectural Terra Cotta and Faience." *Friends of Terra Cotta Newsletter* 1983 (2:3, 10-13).

Fidler, John. "The Conservation of Architectural Terra Cotta and Faience." *Friends of Terra Cotta Newsletter* 1983/4 (2:4, 8-12).

Fidler, John. "The Conservation of Architectural Terra Cotta and Faience." *Friends of Terra Cotta Newsletter* 1984 (3:1, 12-18).

Fidler, John. "The Conservation of Architectural Terra Cotta and Faience." *Friends of Terra Cotta Newsletter* 1984 (3:3, 18-25).

Fidler, John. "The Repair of Architectural Terracotta and Faience--part I" *The Society for the Protection of Ancient Buildings News* 1983 (4:,51-3).

Fidler, John. "Repairing Terracotta, Part II." *The Society for the Protection of Ancient Buildings News* 1984 (5:1, 3,5,7,9).

Fidler, John. "Plenty of Pot." *Traditional Homes* 1987 (3:7, 76-81).

Describes the manufacturing process for architectural detailing.

Fraser, Harry. *Ceramic Faults and Their Remedies.* London: A & C Black, 1986.

This is a very technical book that is aimed at potters. It is not specifically applicable to architectural terracotta.

Ganguli, D. and S. Kumar. *Elements of Ceramic Science.* Calcutta: Indian Institute of Ceramics, 1982.

A technical primer of ceramic science.

Gaskie, Margaret. "The Woolworth Tower: A Technology Revisited, a Landmark Restored." *Architectural Record* 1981 (169:11, 90-95).

Case study of the restoration of the Woolworth Building, glazed terracotta. Looks at replacement materials and cleaning techniques.

Geer, Walter. *The Story of Terra Cotta.* New York: Tobias A. Wright, 1920.

Chronicles terra cotta from antiquity to modern times. Describes contemporary manufacturers as well as the manufacturing process.

Gibson, Bethune M. "Methods of Removing White and Black Deposits From Ancient Pottery." *Studies in Conservation* 1971 (16:2, 18-23).

Deals with two specific types of crusts on objects--not widely applicable for architectural applications.

Gilfillen, Statler. *The American Terra Cotta Index.* Palos Park, IL: Prairie School Press. 1974.

A catalog of the American Terra Cotta Collection, including the history, collections, drawings, architects and photographs of the work performed by several terra cotta companies.

Grimmer, Anne E. *Keeping It Clean: Removing Exterior Dirt, Paint, Stains, and Graffiti from Historic Masonry Buildings.* Washington: U.S. Department of the Interior (National Park Service), 1988.

Good, basic information on cleaning; general soiling, graffiti, paint, and stains. Gives the why along with the how of cleaning.

Hamilton, David. *The Thames and Hudson Manual of Architectural Ceramics.* London: Thames and Hudson, 1978.

This is a manual of ceramics in an architectural context. It examines the varieties of manufacturing processes, and has a wonderful glossary.

Harrison, Douglas. "Renovation of Albert Memorial Bridge." PCI Journal 1989 (34:4).

Case study of bridge restoration. Discusses cleaning and replacement of terracotta.

Heimann, R.B., and U.M. Franklin. "Archeo-thermometry: The Assessment of Firing Temperatures of Ancient Ceramics." *Journal of the International Institute of Conservation (Canadian Group)* 1979 (2:4, 23-45).

Discusses clays in general and changes to clays during the firing process: mineralogical, physical, etc., and how these are used to assess firing temperature.

Hempel, Kenneth. "Notes on the Conservation of Sculpture, Stone, Marble, and Terra Cotta." Brussels: 1967.

Focuses on conservation and deterioration of substrates, and includes only a brief discussion of the formation of the fireskin.

Hoffmann, D. and K. Niesel. "Relationship Between Pore Structure and Other Physico-Technical Characteristics of Stone." *Proceedings of the Eighth International Congress on Deterioration and Conservation of Stone. Berlin, 30 September-4 October, 1996.*

Highlights the interaction between various physical properties, and discusses the need for combination of parameters in testing.

Hunderman, H.J., and Deborah Slaton. "Terra Cotta Restoration, Part I: Organizing the Successful Survey." *Friends of Terra Cotta Newsletter 1984* (3:3, 11-16).

Guidelines for thoroughly surveying a building. Steps include archival research, preliminary inspection, establishing a comprehensive schedule, and finally hands-on inspection.

Irvine, Louise. "Ceramic for a Community." *Glazed Expressions: Tile and Architectural Ceramics Society* 1986 (Summer:12, 1-2).

Describes decorative terracotta and sculpture at Euston Station.

Jester, Thomas C. (ed.). *Twentieth Century Building Materials: History and Conservation.* New York: McGraw-Hill, 1995.

Basic information on history and conservation of terracotta, including deterioration mechanisms, conditions assessment, conservation techniques, and replacement materials.

Jolic, K.I., C.R. Nagarajah, W. Thompson. "Non-contact, Optically Based Measurement of Surface Roughness of Ceramics." *Meas. Sci. Technol 5* (1994).

Optical techniques are considered the best non-contact means of evaluating surface roughness. This article describes a technique for an optically based assessment using a laser.

Jones, John Taylor. *Ceramics: Industrial Processing and Testing,* second edition. Ames: Iowa University Press, 1993.

This is an engineering book that is useful in understanding ceramics as a whole, materials, processes of manufacturing, etc.

Jones, Larry D. "Criteria for Selection of a Most Appropriate Cleaning Method." *Cleaning Stone and Masonry: a symposium.* ASTM Special Publication 935. Philadelphia: ASTM, 1986.

Discusses what, when, and how to clean without harming the substrate.

Kelley, Stephen J. "Preserving Our Past for the Future." *ASTM Standardization News* 1990 (18:12, 28-31).

Report of the ASTM task group for development of standards in the technology of conservation, preservation, and rehabilitation of buildings and structures. Mentions consolidants on masonry; cleaning of masonry, concrete and stucco; repointing historic masonry structures; repairing and replacing terra cotta; surveying structures; and analyzing paints.

Kelley, Stephen J., and Jerry Stockbridge. "The Railway Exchange Building: A Terracotta Renovation." *APT Bulletin* 1988 (20:3, 15-22).

Case study for restoration of glazed terracotta. Good descriptions of the techniques used for in-situ and laboratory evaluation.

Kingery, W.D. *Introduction to Ceramics.* New York: John Wiley, 1976.

This is a fundamental engineering approach to ceramics, but is readable for the novice.

Krouse, Andrew. "The Guaranty Building." *Friends of Terra Cotta Newsletter* 1984 (3:2, 1,5,11).

A description of the process of restoration of the Guaranty building from the perspective of the supplier (Boston Valley)

Kurutz, Gary F. *The Architectural Terra Cotta of Gladding, McBean.* Sausalito: Windgate Press, 1989.

History of Gladding, McBean, with excellent photographs of their work. Photographs by Mary Swisher, introduction by Susan Tunick.

Labine, Clem. "Molded Exterior Ornament." *Clem Labine's Traditional Building* 1991 (4:1, 1, 9-24).

This article contains an excellent sourcelist for terracotta and replacement materials.

Laue, Steffen, Christine Blauer Bohm, and Daniel Jeannette. "Saltweathering and Porosity: Examples from the Crypt of St. Maria im Kapital." *Proceedings of the Eighth International Congress on deterioration and Conservation of Stone. Berlin, 30 September-4 October, 1996.*

Focuses on deterioration due to salts in masonry. Several methods of determining porosity were tested, including mercury intrusion porosimetry,

immersion, and petrophysics. The author concludes that knowing the porous system of a rock its susceptibility towards salt weathering can be explained.

Laurence, F.S. "Terra Cotta in Architectural Design." *Journal of the American Ceramic Society* 1925 (8:2, 79-83).

Terracotta as an artistic and decorative material demands an architecturally educated talent and a ceramic chemist with an appreciation for texture, hue, and color.

Lehmann, Janusz. "The Methodology for the Cleaning and Desalting of Stone Objects in Goluchow Castle Museum." *Preprints of the 8th Triennial Meeting of the ICOM Committee for Conservation,* vol. 2, ed. Kirsten Grimstad, Sydney, Australia 6-11 September 1987. Marina del Rey, CA: Getty Conservation Institute, 1987, 487-91.

Describes the desalinization of stone objects using wet techniques.

Levine, Jeffrey, and Donna Ann Harris. "Stabilization and Repair of a Historic Terracotta Cornice." *APT Bulletin* 1991 (23:3, 48-54).

Describes the process of stabilization of a cornice, focusing on the anchoring system.

Lockhardt, William F. "Architectural Terra Cotta." *General Building Contractor,* January 1931: 52-62.

Describes contemporary manufacturing process form architect's specifications to installation and cleaning.

Loehman, Ronald E. *Characterization of Ceramics.* Boston: Butterworth-Heinemann, 1993.

This is a highly technical book on the characterization of ceramics.

London, Mark. *Masonry: How To Care for Old and Historic Brick and Stone.* Washington: Preservation Press, 1988.

A guide for caring for historic buildings. Topics include preserving a building's character, identifying types of brick and stone, diagnosing masonry problems. cleaning and repointing brick and stone, repairing deteriorated surfaces, and finding and treating moisture problems.

MacIntyre, William A. *Investigations Into the Durability of Architectural Terra Cotta and Faience.* London: Her Majesty's Stationary Office, 1929.

This is an excellent historic source. dealing with the durability of terracotta and its deterioration. There is an extensive section of results of laboratory tests.

Maniatis, Y., and A. Katsanos, M.E. Caskey. "Technological Examinations of Low-Fired Terracotta statues from Ayaia Irini, Kea." *Archaeometry* 1982 (24:2, 191-198).

This study uses SEM and IR spectroscopy to assess the firing temperature of low-fired terracotta statues.

Martin, Lourdes, Miguel Angel Bello, and Antonio Martin. "Accelerated Alteration Tests on the Stones used in the Cathedral of Granada." *Proceedings of the Seventh International Congress on Deterioration and Conservation of Stone.* Lisbon, Portugal, 15-18 June 1992.

Assesses the effects of accelerated weathering tests (crystallization of salts, chemical attack, freeze/thaw included) using SEM, visual observation, and weight change.

Martinek, Ross A. "Criteria for Evaluation of Cleaning Methods of Stone Cladding Materials: The Geological Perspective." *Standards for Preservation and Rehabilitation* (ASTM Special Publication 1258), 1996 pp.367-375.

Highlights the role of the geologist in assessing damage to a masonry surface caused by cleaning.

Mavroyannakis, E.G. "Preliminary Measurements of Thermal Expansion Coefficient of Ancient Terracottas." *Preprints of the 6th Triennial Meeting of the ICOM Committee for Conservation, Ottawa 21-25 September 1981.* Paris: ICOM, 1981.

This article explores the relationship between porosity and thermal expanison. Unfortunately, the poor translation renders it almost unintelligible.

Meadows, Robert E. *Historic Building Facades: A Manual for Inspection and Rehabilitation.* New York: New York Landmarks Conservancy, 1986.

As the title states, a how-to manual for inspection and rehabilitation.

Mel'Nikova, E.A., and M.N. Lebel. "Application of Polymer Films Removing Surface Contamination from Sculptures made of Different Materials." *Preprints of the 5th Triennial Meeting of the ICOM Committee for Conservation, 1-8 October 1978, Zagreb.* Paris: ICOM, 1978, 6.

This is a preliminary report on the use of polymer films to remove soiling from sculpture of different composition. A follow up study had not been published.

Middleton, Andrew, and Ian Freestone. *Recent Developments in Ceramic Petrology.* London: British Museum, 1991.

A solid knowledge of petrology is required to use this report.

Moynehan, C.R. et al. "Surface Analysis of Architectural Terracotta." *Journal of Architectural Conservation* 1995 (1:1, 56-69).

Use of many analytical techniques to assess damage done: SEM, XRD, AAS, and others. Found that HF removes silicates of the fireskin.

Murray, M.J. and R.N. Butlin. "Atmospheric Decay and Cleaning of Historic Architectural Terracotta." *Preservation and Restoration of Cultural Heritage: Proceedings of the 1995 LCP Congress, Montreaux, 24-29 September 1995.* 1996 p.429-437.

National Park Service. *Historic Masonry Deterioration and Repair Techniques: An Annotated Bibliography.* Washington: U.S. Department of the Interior, 1993.

This bibliography is a good resource, but is becoming dated.

Naude, Virginia Norton. "Conservation of Six Terracotta Portrait Busts by William Rush." *Preprints of Papers presented at the Eleventh Annual Meeting of the American Institute for Conservation of Historic and Artistic Works.* Baltimore, Maryland, 25-29 May 1983, 86-96. Washington: AIC, 1983.

This article describes a cleaning system for terracotta busts that involves immersion in water. While it was effective for this application, it is not generally applicable to architectural terracotta.

Ontario Ministry of Citizenship and Culture. *Annotated Master Specifications for the Cleaning and Repointing of Historic Masonry.* Toronto: 1985.

Very specific guidelines for the cleaning of historic masonry. Gives good sense of the state of the cleaning field at the time.

Orphanides, Andreas G. *Radioanalytical Techniques in Archaeology: Pottery and Raw Clay Analysis.* Nicosia, Cyprus: Ago Publications, 1985.

Describes the analytical techniques used in characterization of ancient potteries in very simple terms. SEM, XRD, and others are discussed.

Perez, J.L., C. Maqueda, and A. Justo. "A Scientific Study of the Terracotta Sculptures from the Porticoes of Seville Cathedral." *Studies in Conservation* 1985 (30:1, 31-38).

A characterization of the sculptures in question. It was determined that two firing temperatures were used, and the mineralogical composition of the terracotta was determined.

Prudon, Theodore H.M. "Architectural Terra-Cotta: Analyzing the Deterioration Problems and Restoration Approaches." *Technology and Conservation* 1978 (3:3, 30-38).

This article describes the use of architectural terracotta and the processes surrounding it including specification, manufacturing. Deterioration patterns of terracotta including crazing and bond failure of glazes, differential stresses, freeze/thaw, and crystallization of salts. Discusses the importance of understanding deterioration mechanisms in designing a restoration plan.

Reedy, Chandra. "Thin-Section Petrography in Studies of Cultural Materials." *Journal of the American Institute for Conservation* 1994 (33:2, 115-129).

Discusses the underutilized technique of thin section petrography in the analysis of conservation treatments on cultural objects. Thin sections can be used to identify inorganic minerals, locate the specific source of minerals, and group objects of a common source. Many materials are discussed, including terracotta sculpture.

Rice, Prudence. *Pottery Analysis: a Sourcebook.* Chicago: University of Chicago Press, 1987.

This is the definitive source on pottery. Particularly useful for terracotta in terms of characterization.

Rincon, Jesus, and Maximina Romero. "Archeometric Characterization of 'Terra Sigillata' Ceramics." *The Ceramics Cultural Heritage, ed. P. Vicenzini. Proceedings of the International Symposium The Ceramics Heritage of the 8th Cimtec World Ceramics Congress and Forum on New Materials, Florence, Italy, June 28-July 2, 1994.* Faenza: Techna, 1995. 325-330.

This article demonstrates the used of characterization techniquesfrom materials science, including XRD, SEM/EDX (energy dispersive x-ray).

Rogers, Anne, and Doyle Wilhite. "Exterior Restoration of the West Virginian State Capitol: Cleaning and Structural Stabilization Procedures." *Technology and Conservation* 1979 (4:1, 14-16).

This is a case study of the restoration of a terra cotta building. Cleaning procedure was water washing at 250 psi.

Ross, K.D., D. Hart, R.N. Butlin. "Durability Tests for Natural Building Stone." *Durability of Building Materials and Components. Ed. J.M. Baker, P.J. Nixon, A.J. Majumdar, and H. Davies. Proceedings of the Fifth International conference held in Brighton, U.K., 7-9 November 1990.*

This is an easy-to-read article that discusses causes of stone decay. It gives good, clear explanations of the actual deterioration mechanisms which include frost, crystallization of salts, and acid deposition.. Factors influencing durability (pore structure and mineralogy), were discussed, and various tests used to assess durability (saturation coefficient, acid resistance, freeze/thaw tests, crystallization tests) were outlined.

Rossi Manaresi, Rafaella, and Giorgio Torraca. *The Treatment of Stone: Proceedings of the Meeting of the Joint Committee for the Conservation of Stone, Bologna, October 1-3, 1971. (ICOM, ICOMOS, International Centre for Conservation, Working Group on the Treatment of Stone).* Bologna: Centro per la Consevazione delle sculpture all'aperto, 1972.

This is a collection of articles regarding the treatment of stone. Nothing specifically oriented toward terracotta cleaning is included.

Rossi Manaresi, Rafaella. *Conservation Works in Bologna and Ferrara: Case studies in the Conservation of Stone and Wall Paintings.* Bologna: Fondazione Internazionale Cesare Gnudi, 1986.

This is a collection of articles regarding the treatment of stone. Nothing specifically oriented toward terracotta cleaning is included.

Roth, Ron. "Masonry Building Materials." *Brownstoner* 1985 (16:1, 1-6).

A very basic discussion of terracotta including history, use, manufacturing process and character. This is part of a larger article on masonry building materials.

Rudder, T.H. "Chemical Cleaning of Historic Structures: A Practical Approach." *Cleaning Stone and Masonry: a symposium.* ASTM Special Publication 935. Philadelphia: ASTM, 1986.

This article outlines the reasons for cleaning a building, including aesthetics, exposure of the substrate for evaluation and repair, removal of damaging pollutants, and unclog the clogged pores of the building to allow for the normal transpiration of moisture. Recommends chemical cleaning, but uses only visual observation only in assessing damage to substrate.

Saleh, Saleh A., Fatima Helmi, Monir M. Kamal, and Abdel-Fattah E. El-Banna. "Artificial Weathering of Treated Limestone: Sphinx, Giza, Egypt." *Proceedings of the Seventh International Congress on Deterioration and Conservation of Stone.* Lisbon, Portugal, 15-18 June 1992.

Investigated the effects of artificial weathering agents on treated limestone. Loss of mass and SEM were used to assess change.

Sarring, Kevin Lee, and Theresa Ducato. "Material Matters: Terracotta, Limestone, and Brick: Timeless Terracotta." *Inland Architect* 1984 (28:2, 14-25).

This article is a general description of terracotta, including history of use, manufacturing process, classification (into the categories of brownstone, fireproof construction, ceramic veneer, and glazed architectural terracotta) deterioration mechanisms, and very basic conservation techniques.

Schachtman, Alan. "Renovating Chicago's Reliance Building." *Urban Land* 1996 (55:2, 13, 42, 44).

Case study of glazed terra cotta renovation.

Schubert, P. "Petrographic Modal Analysis: A Necessary Complement to Chemical Analysis of Ceramic Coarse Ware." *Archaeometry* 1986 (28:2, 163-178).

Discusses the power of and need for petrography as used for the provenance of pottery.

Searls, C.L. and S.E. Thomasen. "Repair of the Terracotta Façade of Atlanta City Hall." *Structural Repair and Maintenance of Historic Buildings, vol. 2.* Southampton: Computational Mechanics Publications, 1991. 245-257.

Case study: examines the failures of terracotta on Atlanta City Hall, and attributes causes after laboratory analysis. Summarizes the restoration process, but does not discuss cleaning.

Slaton, Deborah and Mark Morten. "Issues in the Salvage and Reuse of Terracotta: two case studies." *Standards for Preservation and Rehabilitation* (ASTM Special Publication 1258), 1996 pp.307-318.

Case studies: the cleaning system employed was an alkali prewash with an acidic afterwash, but not discussed in detail.

Smith, Julia A. "Decorating a Revival." *Country Life* 1990 (184:44, 94-96).

This is a brief article that hits the highlights of terracotta: history of use in England, the manufacturing process, cleaning mistakes, replacement, and current use.

Spry, Alan. "Principles of Cleaning Masonry Buildings." *Technical Bulletin 3.1.* Melbourne: National Trust of Australia (Victoria, 1982).

A thorough examination of cleaning, including reasons for cleaning the nature of soiling, different kinds of substrates, and various cleaning methods.

Spurrier, H. "Some Fundamentals of Terra Cotta." *Journal of American Ceramic Society* 1928 (9: 773-8).

Terra cotta is not a definite material, and considerable differences of opinion as to the ideal composition exist. A fuller knowledge of the fundamentals will result in a better product. Character and size of grog is discussed.

Stelzer, David. "The Chemistry of Color Matching." *Clem Labine's Traditional Building* 1996 (9:3, 72-82).

Focuses on the techniques available for color matching, but has an excellent supplier chart for terracotta and replacement terracotta products.

Stockbridge, J.G. "Evaluation of Terra Cotta on In-Service Structures." *Durability of Building Materials and Components. Proceedings of the First International Conference, Ottawa, 21-23 August 1978* (ASTM Special Publication 691). Philadelphia: ASTM, 1980. 218-230.

Discusses problems of terra cotta construction, including issues due to design and improper inspection. Outlines important techniques in evaluation and determination of weakness in terra cotta units.

Stockbridge, Jerry G. "Analysis of In-Service Architectural Terra Cotta." *APT Bulletin,* (18:4, 41-5).

Essentially, a summary of the above.

Stratton, Michael. "The Nature of Terracotta and Faience." *Architectural Ceramics*, ed. Jeanne Marie Teutonico. A Joint Symposium of English Heritage and the United Kingdom Institute for Conservation, 22-25 September 1994. London: James and James, 1996, 45-54.

Brief history of the use of architectural terracotta in Britain and North America.

Stratton, Michael. *The Terracotta Revival: Building Innovation and the Image of the Industrial City in Britain and North America.* London: Victor Gollancz with Peter Crawley, 1993.

A comprehensive history of the use of terracotta in Britain and North America.

Sweet's General Building and Renovation Catalog. New York: Sweet's Group, 1993.

Outlines terracotta products currently on the market. Some entries give technical information including performance standards.

Taylor, James. "Terra Cotta--Some of its Characteristics." *Technology and Conservation* 1992 (11:1, 15-17).

Article reprinted from 1891. Historical perspective on the use of terracotta and its characteristics.

Ternbach, Joseph. "A Sixteenth Century Terra Cotta Statue: Problems of Restoration and Preservation." *Curator* 1959 (2:3, 219-232).

Case study of restoration of a statue. Discusses the process of discovery and restoration of the statue, no substantial discussion of cleaning.

Teutonico, Jeanne Marie. *Architectural Ceramics: A Joint Symposium of English Heritage and the United Kingdom Institute for Conservation, 22-25 September 1994.* London: James and James, 1996.

An excellent collection of the most recent research on architectural ceramics.

Thomassen, Sven. "Inspecting, Testing, and Analyzing Terracotta." *Friends of Terra Cotta Newsletter* 1982 (1:3, 3-4).

Primarily regarding inspecting for deterioration, but discusses important

techniques and tests for identifying the material's properties.

Timms, Joseph. "Architectural Terra-Cotta." *The Brickbuilder* 1893 (2:1, 1-3; 2:2, 1-14; 2:3, 21-24.).

Timms, Joseph. "Terra-Cotta and Faience as Materials for Architectural and Decorative Applications." *The Brickbuilder* 1893 (2:3, 34-6; 2:4, 48-9).

Tindall, Susan. "How To Prepare Project-Specific Terra-Cotta Specifications." *APT Bulletin* 1989 (21:1, 26-36).

Discusses standards for terra cotta, both past and present. Due to its varied nature, identifies properties that it is important to evaluate, including compressive strength, modulus of elasticity, shear strength, flexural strength, expansion coefficients, absorption, and hardness.

Tindall, Susan. "Egyptian Theater." *Friends of Terra Cotta Newsletter* 1983 (2:3, 14-15).

Case study of the restoration of the Egyptian Theater (glazed terracotta).

Torraca, Giorgio. *Porous Building Materials: Materials Science for Architectural Conservators.* Rome: ICCROM, 1982.

A primer of porous building materials for architectural conservators.

Tunick, Susan. *Terra Cotta: Don't Take it for Granite!* New York: Friends of Terra-Cotta Press, 1995.

Three walking tours for terracotta aficionados in New York City.

Tunick, Susan. "The Reign of Terra Cotta in the United States: Enduring in an Inhospitable Environment, 1930-1968." *APT Bulletin* 1998 (29:1, 43-48).

Discusses the dearth of terracotta in architecture during the mid-twentieth century.

Tunick, Susan. *Terra Cotta Skyline: New York's Architectural Ornament.* New York: Princeton Architectural Press, 1997.

A comprehensive book on terra cotta in the United States with beautiful photography by Peter Mauss. History, manufacturing, and design are all discussed.

U.S. Bureau of Standards. "Cleaners for Terracotta." *National Bureau of Standards Technical News Bulletin* 1928 (131:32-33).

Evaluates several cleaners used for both glazed and unglazed terracotta in 1928. Cleaners evaluated include sodium hydro-sulfite, fluosilic acid, tri-sodium phosphate, soap powder, hydrochloric acid, and hydrofluoric acid. HF removed the dirt better than any other cleaner but etched the surface finish quite badly.

VanArdt, Johannes H.P., and Petrus J. Loubser. "External Wall Tiling: Problems and Suggested Tiling Procedures." *RILEM/ASTM/CIB Symposium on Evaluation of the Performance of External Vertical Surfaces of Buildings. Otaniemi, Finland. 28-29 August, 1977.* Helsinki: Technical Research Center of Finland, 1978, 13-21.

Discusses problems of adhesion of tiles. Not specifically relevant to architectural terra cotta.

Wallasch, S., F. Schlutter, H. Juling, and R. Blaschke. "Weathering and Conservation of North German Terracotta." *Conservation of Historic Brick Structures: Case Studies and Reports of Research.* Dorset: Donhead, 1998. (347-359).

Weaver, Martin E. with Frank G. Matero. *Conserving Buildings: Guide to Techniques and Materials,* revised edition. New York: John Wiley and Sons, 1997.

Excellent secondary source. Includes history, manufacturing process, essential properties, cleaning techniques, replacement, etc.

Werner, M. "Changes of Surface Characteristic of Sandstone caused by Cleaning Methods Applied to Historical Stone Structures." Ed. J.M. Baker, P.J. Nixon, A.J. Majumdar, and H. Davies. *Proceedings of the Fifth International conference held in Brighton, U.K., 7-9 November 1990.*

Effects of twelve different cleaning methods were investigated for the changes induced in capillary absorption, change in depth profile, change of color, and determination of the loss of substance. It was concluded that the degree of weathering of the stone had a greater influence than the applied cleaning method.

West, H.W.H, R.W. Ford, and F. Peake. "A Panel Test for Freezing Brickwork." *Transactions and Journal of the British Ceramic Society* 1984 (83:4, 112-5).

Describes a method for performing a freeze/thaw test on only one surface of a brick surface. Requires specialized apparatus.

Wilson, Forrest. *Building Materials Evaluation Handbook.* New York: Van Nostrand Reinhold, 1984.

Brief discussion of the use of terracotta, then outlines common problems and deterioration mechanisms. Describes various methods of inspection, including tapping, infrared scanning, sonic testing, metal detection, and laboratory analysis. Further discusses deterioration mechanisms common to masonry in general.

"Gladding, McBean and Co." *Friends of Terra Cotta* 1981 (1:1, 6-8).

Gives a general history of the company.

"Technical Notes." *Friends of Terra Cotta Newsletter* 1984 (3:2, 12-13).

In response to John Fidler's series of articles. Reiterates the importance of not sandblasting.

"Terra-Cotta in Architecture." *The California Architect and Building News* 1884: November, 200+.

Discusses the improvement that terracotta offers as a building material. Pages of pictures of contemporary details available from Gladding, McBean are included.

"Architectural Terra Cotta and Faience." *Brick and Clay Record* 32 (January 1910): 135-6.

Discusses the properties of terra cotta and faience, distinguishes between them.

"Cleaning Brick Masonry." *Technical Notes on Brick Const*ruction 20 (Sept. 1977, rev. June 1987).

Describes various methods for cleaning brick. Cleaning of brick is a trial and error procedure: testing should be performed to assess the effect of the method chosen. Keeping a building clean during construction is more effective than cleaning later on.

PRODUCT DATA

RESTORATION CLEANER

SURE KLEAN

DESCRIPTION AND USE

Sure Klean® Restoration Cleaner is a concentrated compound formulated as a "carbon solubilizer". Used properly, it cleans brick, granite, sandstone, terra cotta, exposed aggregate and other masonry except limestone, marble or concrete. This product has been safely and effectively used to clean historic structures throughout the United States and Canada.

Sure Klean® Restoration Cleaner, when properly used, is safer and less expensive than sandblasting or steam cleaning. Application to masonry surfaces loosens and dissolves dirt, paint oxidation, carbon buildup and other atmospheric pollutants. A simple cold water rinse then removes these unsightly stains.

ADVANTAGES

- **Proven effective for cleaning dirty and heavily carboned buildings.**

Restoration Cleaner recommended for these substrates. Always test.

Architectural Concrete Block	Smooth	no	N/A
	Split-faced	no	
	Burnished	no	
	Ribbed	no	
Concrete	Brick	no	N/A
	Tile	no	
	Precast Panels	no	
	Pavers	no	
	Cast-in-place	no	
Fired Clay	Brick	yes	125-400 sq/ft 12-37 sq/m
	Tile	yes	
	Terra Cotta	yes	
	Pavers	yes	
Marble, Travertine, Limestone	Polished	no	N/A
	Unpolished	no	N/A
Granite	Polished	yes	200-500 sq/ft 19-47 sq/m
	Unpolished	yes	200-500 sq/ft 19-47 sq/m
Sandstone	Unpolished	yes	125-400 sq/ft 12-37 sq/m
Slate	Unpolished	yes	200-500 sq/ft 19-47 sq/m

May have limited effectiveness on highly porous surfaces. Always test to ensure desired results. Coverage estimates depend on surface texture and porosity.

- **Safer than sandblasting. Will not pit or damage the masonry when properly applied.**

Limitations

- Not suitable for cleaning of limestone, concrete or marble surfaces. See Sure Klean® Limestone Restorer or 766 Limestone & Masonry Prewash/Afterwash for these applications.
- Not recommended for interior use. Contact PROSOCO's Customer Service for recommendations for the most appropriate Sure Klean interior cleaning system.
- May not be suitable for some polished stone and "glazed" surfaces. Always test.

TECHNICAL DATA

FORM: Clear liquid
SPECIFIC GRAVITY: 1.050
FLASH POINT: None
pH: 3.0 (@ 1:5 dilution)
WT./GAL.: 8.75 lbs.

PREPARATION

Protect

Restoration Cleaner is corrosive, etches glass and architectural aluminum and is harmful to wood, painted surfaces and foliage. **BEWARE OF WIND DRIFT.**

Complete masonry cleaning before replacement of windows, doors, hardware, light fixtures, roofing materials, wood and any other nonmasonry items which may be damaged by the cleaning product. If such fixtures have been installed or are to remain in place, protect before overall application using Sure Klean® Strippable Masking (where appropriate according to product literature) or polyethylene. Be sure that all caulking and sealant materials are in place and thoroughly cured before cleaning begins.

Protect surrounding metal, painted surfaces, wood, adjacent plant life and all other nonmasonry materials from exposure to the cleaning solution. Take precautions to protect building occupants,

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pedestrians and nearby property from contact with the cleaner, rinse waters or fumes.

Beware of drifting of sprayed material or rinse water. Pedestrian and auto traffic must be diverted or protected. When working over traffic, clean only when traffic is at a minimum and protect carefully.

Surface & Air Temperatures
To avoid harm to masonry, do not clean when temperatures are below freezing or will be overnight. Best cleaning results are obtained when air and masonry surface temperatures are 40ûF (4°C) or above. If freezing conditions exist prior to application, allow adequate time for masonry to thaw.

When cleaning glazed terra cotta and tile, inspect the surface carefully. Where glaze has been partially weathered away or previously etched, cleaning may cause additional loss of glaze.

APPLICATION INFORMATION

Before applying, read "Protect" in Preparation section and "Precautionary Measures" under Safety Information.

Pretesting
ALWAYS TEST (minimum 4 ft. x 4 ft. (1.2 m x 1.2 m) area) prior to beginning full-scale cleaning operations to determine dilution rate and compatibility with masonry surfaces. Test each surface and each type of stain. Also test to see what effect pressure rinsing may have on older masonry. To evaluate final appearance and results, allow test panels to dry three to seven days before inspection and make available for inspection and approval before proceeding with overall cleaning.

Dilutions
Porous masonry — Use concentrate during initial testing. If concentrate cleans effectively, tests should be run with diluted solutions of up to three parts water to one part concentrate. Use the mildest solution that effectively cleans depending upon test results.

Nonporous masonry (glazed brick, terra cotta, polished granite) — dilute with one to three parts water to one part concentrate, depending on test results. Sure Klean® Restoration Cleaner is an acidic product and may etch polished and glazed surfaces. Care should be taken particularly on polished granite. The extent of etching can be controlled by dilution.
When diluting, always pour water into empty bucket first, then carefully add concentrate. Handle in rubber or polyethylene buckets only. Acidic liquids and fumes will attack metal.

Application Instructions
1. After protecting all nonmasonry surfaces, thoroughly wet the area to be cleaned.
2. Apply the cleaning solution liberally using low pressure spray (50 psi), roller or densely filled (tampico) masonry washing brush.
3. Allow the cleaning solution to remain on the surface for 3-5 minutes. Reapply. Light scrubbing of the surface will improve cleaning results especially where high pressure rinsing equipment is not available. If the cleaning solution is left on the surface unattended, take precautions to prevent pedestrians from coming near treated surfaces.
   Caution: Do not allow cleaning solution to "dry in" to the masonry – bleaching may occur.
4. Begin rinsing with low pressure, flood rinse to remove initial acidic residue with minimum risk of wind drift. Then rinse the treated area thoroughly using high-pressure spray. Rinse from the bottom of the treated area to the top flushing each section of the surface with a concentrated stream of water. To avoid streaking on vertical walls, take care to keep the wall below wet and rinsed free of cleaner and residues.

Note: Application of rinse water is extremely important to assure that all surface staining matters and cleaning residues are thoroughly flushed from the treated surface. Pressure rinsing equipment with 600-1000 psi and 15-30 degrees fan tip will prove most effective. Older, more delicate masonry may require restricting water pressure to avoid damage.

DO NOT APPLY RESTORATION CLEANER WITH HIGH PRESSURE SPRAY. Such application will drive the chemicals deep into the surface, making it difficult to rinse completely. Discoloration to the surface may result.

When cleaning severely stained areas such as horizontal surfaces, under window sills, eaves, etc., "pretreating" the surface with Sure Klean® 766 Limestone & Masonry Prewash may prove more effective. Read and follow product procedures and recommendations. Pressure rinse, then "afterwash"

with Sure Klean® Restoration Cleaner followed by water rinse.

Application of good "breathable" water repellent to the cleaned masonry surface reduces absorption of stain-producing elements, keeping the surface clean for a longer period of time and making future cleaning operations faster and easier. For more information about water repellents for various masonry surfaces, contact PROSOCO's Customer Service (see next page) regarding Sure Klean® Weather Seal products.

SAFETY INFORMATION

DANGER! POISON!
Causes Severe Burns Which May Not Be Immediately Painful Or Visible
Harmful Or Fatal If Swallowed Or Inhaled
For Use By Professional Applicators Only
Keep Out Of The Reach Of Children
Read Precautionary Measures Carefully

Precautionary Measures
Contains hydrofluoric acid. Do not get in eyes, on skin or clothing. Avoid breathing fumes and contact with mucous membranes. Keep container tightly closed when not dispensing product. Use with adequate ventilation.

Wash thoroughly after handling. Wear rainsuit of plastic, rubber or PVC, rubber boots and gloves, face shields and goggles to avoid splash to bare skin or eyes and NIOSH/MSHA approved respirators for use with acids.

Avoid exposing building occupants to fumes. When applying outside occupied buildings, all windows, air intakes and exterior air conditioning vents should be covered (and air handling equipment shut down) during and for 30 minutes following application. Dispose of empty containers according to federal, state and local regulations.

Use well- maintained staging and scaffolding equipped with steel cable. Acidic materials will attack nylon, cotton or hemp rope. Use polypropylene ropes and safety lines. Avoid drifting of sprayed material or rinse residues onto autos and pedestrians by protecting or diverting such traffic. Do not alter, mix with chlorine-type bleaches or other chemicals or dilute product except as specified. Do not use for applications other than specified. Read Material Safety Data Sheet for additional safety and health hazard information.

First Aid Instructions
Eye Contact: Immediately flush with plenty of water for at least 30 minutes, keeping eyelids apart and away from eyeballs during irrigation. If physician is not immediately available, apply 1 or 2 drops of 0.5% Pontocaine Hydrochloride solution followed by a second irrigation for 15 minutes. **DO NOT** use solution described for skin treatment. Get medical attention immediately, preferably an eye specialist.
Skin Contact: Immediately place under a safety shower or wash the burned area with a water hose for a minimum of 15-20 minutes. Remove all contaminated clothing. After washing, immerse burned area in solution of 0.13% Zephiran® Chloride. Seek medical attention immediately.
Inhalation: Immediately remove to fresh air. If breathing stops, give artificial respiration, but **not** mouth-to-mouth. If breathing is difficult, give oxygen. Get medical attention.
Ingestion: Do **not** induce vomiting! If victim is conscious, give large quantities of milk or water. Never give anything by mouth to an unconscious person. Get medical attention.

Fire and Explosion Hazard Data
Contact with metals produces extremely flammable and explosive hydrogen gas.

Spill or Leak Procedures
Wear acid-resistant protective clothing and complete protective equipment. Contain the spill and neutralize with soda ash or lime. Recover neutralized material for disposal according to local, state and federal regulations. Provide adequate ventilation.

Container Handling and Storage
Store upright in a cool, dry place. Store away from all other chemicals and potential sources of contamination. Keep lights, fire and sparks away from container. Keep container tightly closed when not dispensing product. Do not use pressure to empty container. Wash thoroughly after handling. Do not drop onto or slide across sharp objects. Do not use container as dilution or mixing vessel. Do not cut, grind or weld on or near this container. Empty containers retain residue and vapors and must be handled as if full.

Shelf Life
Shelf life is 3 years from date of manufacture when product is in a tightly sealed, unopened container.

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WARRANTY

The information and recommendations made are based on our own research and the research of others, and are believed to be accurate. However, no guarantee of their accuracy is made because we cannot cover every possible application of our products, nor anticipate every variation encountered in masonry surfaces, job conditions and methods used. The purchasers shall make their own tests to determine the suitability of such products for a particular purpose.

PROSOCO, Inc. warrants this product to be free from defects. **Where permitted by law, PROSOCO makes no other warranties with respect to this product, expressed or implied, including without limitation the implied warranties of merchantability or fitness for particular purpose.** The purchaser shall be responsible to make his own tests to determine the suitability of this product for his particular purpose. PROSOCO's liability shall be limited in all events to supplying sufficient product to re-treat the specific areas to which defective product has been applied. Acceptance and use of this product absolves PROSOCO from any other liability, from whatever source, including liability for incidental, consequential or resultant damages whether due to breach of warranty, negligence or strict liability. This warranty may not be modified or extended by representatives of PROSOCO Inc., its distributors or dealers.

CUSTOMER SERVICES

Factory personnel are available for product, environment and job-safety assistance with no obligation. Call 913-281-2700 and ask for Customer Service.

Factory-trained representatives are established in principal cities throughout the continental United States. Call Customer Service, 913-281-2700, and request the name of the Sure Klean® representative in your area.

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